

Synthesis and Characterization of High Tg Nanofoams Based on Pyromellitic Dianhydride and 1,1-Bis(4-Aminophenyl)-1-Phenyl-2,2,2-Trifluoroethane Polyimide Block and Graft Copolymers

by

Saikumar Jayaraman

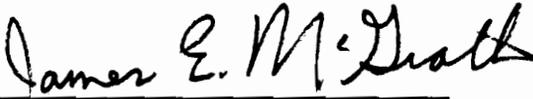
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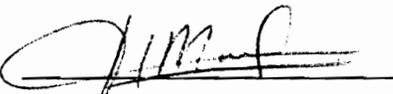
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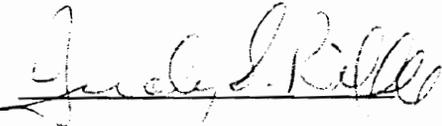
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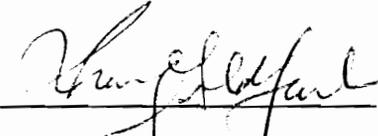
Dr. Harry W. Gibson



Dr. Herve Marand



Dr. Judy S. Riffle



Dr. Ivan J. Goldfarb

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Saikumar Jayaraman

Committee Chairman: James E. McGrath
Chemistry

(Abstract)

Thermally stable polyimide block and graft copolymers with labile components (especially polypropylene oxide), have been prepared and investigated as low dielectric materials that afford desirable thermal, mechanical and electrical properties. Polyimide nanofoams based upon the controlled pyrolysis of the labile component were prepared. The methodology for producing the nanofoams was to first spin cast well-designed microphase separated graft or block copolymer solutions comprised of the thermally stable 1,1-Bis(4-aminophenyl)-1-phenyl-2,2,2-trifluoroethane (3FDA)/pyromellitic dianhydride (PMDA) based polyimide main chain and polypropylene oxide based thermally labile graft or block copolymers. The thermally stable material was designed to be the continuous phase, and the unstable moiety served as the dispersed phase so that closed cell structures could be obtained. Upon thermal treatment under inert atmosphere, the materials can be spun cast and cured in place, if so desired. However, if the polymers are exposed to the oxygen atmosphere, the unstable component can be selectively degraded, generating micropores that are related to the size of the initial microphase separated copolymer morphology.

The copolymer synthesis was conducted through the poly(amic acid) precursor and subsequent cyclodehydration to the polyimide, usually by chemical imidization. Dynamic mechanical analysis (DMTA) confirmed microphase separated morphology for all the copolymers. Upon degradation of poly(propylene oxide), a 13-18% reduction in the density was observed, which is consistent with foam generation. These features have been confirmed using small angle X-ray analysis (SAXS) and transmission electron microscopy (TEM). The pores ranged from 100-250^oA in size from TEM, and were stable up to nearly the polyimide Tg (~400^oC).

Related efforts demonstrated that it was possible to introduce ethynyl containing terminal groups, in order to develop crosslinked polyimide foams with better chemical resistance. In addition to the propylene oxide labile components, poly(methyl methacrylate) and polyethylene oxide were also investigated. Macromonomers were synthesized via group transfer polymerization, followed by a derivatization to produce appropriately reactive diamino aryl terminal oligomer. Surprisingly, the poly(methyl methacrylate) component was found to be miscible with 3FDA/PMDA based polyimide. Indeed, even physical blends of the two homopolymers appear to be miscible. Polyethylene oxide has also been tried as a labile block for the generation of polyimide nanofoams, with only limited success.

The optimum resulting materials are of considerable further interest for electronic packaging applications where air is utilized as a component to reduce the dielectric constant.

This body of work is dedicated to my parents, my wife, and my undergraduate professor,
Dr. B.R. Ramachandran

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1.0 - INTRODUCTION

The synthesis and evaluation of new, thermally stable polymers developed into a major worldwide effort in the decade of the 1950's and the 1960's. Pioneering research in this area was conducted to satisfy the demands of the advanced aircraft, weapons and electronics industries. Appropriate materials required processability, but also had to satisfy stringent performance requirements, including performing under severe static and cyclic loading cycles, harsh environments such as high energy radiation, strong magnetic and electrical fields, aggressive solvents and high temperatures. Moreover, certain applications for these materials had to maintain structural integrity for thousands of hours of continuous operation at temperatures such as 230°C, and possibly for a few seconds at temperatures as high as 760°C.¹

The greatest success was achieved with polymers containing aromatic or heterocyclic rings (normally in combination) in the main chain backbone such as poly(phenylenes)², Poly(benzothiazoles)³, poly(benzimidazoles)⁴, poly(phenyl quinoxalines)⁵, poly(phenylene sulfides)⁶ and aromatic polyimides⁷. Because of problems arising through poor availability of starting materials and difficulties in synthesis or processing, relatively few of these polymers achieved commercial viability. Polyimides were the most successful in demonstrating useful technological properties and processability, coupled with very high heat resistance. Since the early 1960's, the search for new, thermally stable polymers has diminished quite significantly and recent efforts have concentrated upon improved methods for the synthesis of known structures, or upon modifications to these structures to improve fabricability, with minimum loss in thermal stability. This has been especially true for the polyimides, which now make up approximately 40% of the named commercially available heat resistant, nonmetallic

materials for use at temperatures up to 300°C. Both addition chain cure type and high molecular weight thermoplastics produced via polycondensation reaction, are produced and marketed as films, molding powders, wire coating enamels, adhesives, laminating resins, fibers and, to some extent, as foams.

Since their introduction in 1926⁸, polyimides have become one of the important materials in the microelectronics industry. Their usefulness to this industry was realized very early, for example, as a plastic insulator that could retain both electrical and mechanical characteristics at temperatures in excess of 250°C.⁹ The Kapton, polyimide was commercialized by DuPont in 1970 and is often the polymer of choice. Later Harada and coworkers at Hitachi Central Research Laboratories developed a polyisoindoloquinazolinedione, (given the acronym PIQ), which was suitable as an insulator for multilayered interconnections on large scale integrated circuit (LSI) surfaces, as well as a passivation overcoat film.¹⁰ Rubner and coworkers described a photosensitive polyimide that was expected to shorten the semiconductor processing steps.¹¹ Rothman was the first author to evaluate and compare commercially available polyimide resins by testing their characteristic, vital to their use in LSI and very large LSI(VLSI)¹² circuits. Thus, various characterization tests of polyimides have resulted in their use as inter level dielectric's, passivation layers, barrier layers, adhesives, encapsulants and as fabrication aids. Since 1983, the sales of polyimides for electronics have increased considerably, in spite of the prejudice and belief of many in industry which have historically been very resistant to change. Thus organic materials, along with inorganic materials, have been well accepted and are being used in microelectronic devices.

The continued expansion of the "information era," has resulted in a need for faster, more dense, low cost chips and packages, resulting in a need for the tools, materials, processes and facilities to fabricate them. The explosion in density and performance that has occurred since 1960 has been highly dependent on the polymers used to define the

circuitry, encapsulate the chips and package the system. The future of polyimides in the microelectronics area is expected to revolve not only around developing new polyimides, but preferably in modifying existing polyimides. There is expected to be a continued reliance on new radiation sensitive polyimide materials for advanced optical, E - beam and X ray lithography application, low dielectric constant and low coefficient of thermal expansion polyimides for packaging applications. Other major goals are to make the chips process faster, to make the devices smaller and lighter, and finally to fabricate them at a lower cost.

This dissertation focuses on a novel approach to decrease the dielectric constant of the polyimide to a value of 2 or less, while maintaining their thermal stability and desirable mechanical properties. Incorporating fluorine in polyimides has been used in the past to lower the dielectric constant. However, a different approach to substantially reduce the dielectric constant, while maintaining the desired thermal and mechanical properties of the polyimides would be to generate a foamed morphology. A reduction in the dielectric constant could here be achieved by replacing the polymer matrix with air pockets that have a dielectric constant of 1. Although the concept of polyimide foams has existed for quite some time, current aerospace and transportation industries utilize either foaming agents, inclusion of microspheres, or partial degradation of the polymer to generate a foam. However, most of these high temperature foams have characteristic void or cell sizes that are large (generally in the tens of microns), which is highly impractical for the area of thin film applications. This dissertation deals with the development of polyimide foams having a pore size in the nanometer regime by using the concept of microphase separated polyimide block or graft copolymers, wherein the copolymer is comprised of a thermally stable polyimide block, with a thermally labile block or graft as the dispersed phase. Upon thermal treatment, the hypothesis was that the thermally unstable dispersed phase would

undergo thermolysis, leaving micropores whose pore size and shape are dictated by the initial copolymer morphology.

Chapter Two deals with a literature review of the synthesis, characteristics and application of polyimides concentrated toward the microelectronics industry. This chapter also provides a short overview on the various methods used to generate polyimide foams. Chapter Three discusses the synthetic and analytical experimental methods, both used in this research. A discussion of the experimental results is presented in Chapter Four, followed by Conclusions and References.

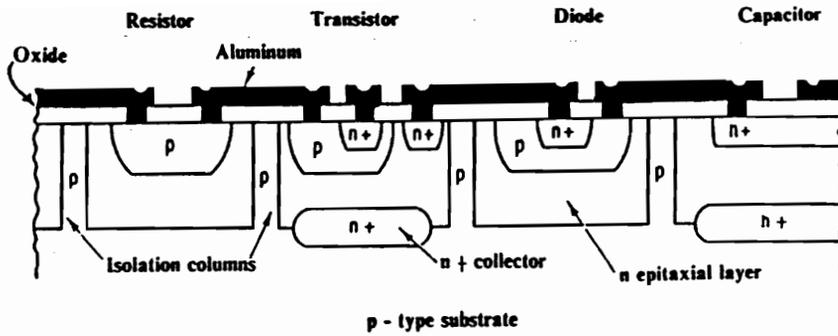
2.0 - LITERATURE REVIEW

With the birth of the "information age" , this century has witnessed an electronics revolution that has made microelectronics a part and parcel of our lives. Since the mid-1940's, with the invention of bipolar transistors by Shockley, Bardeen and Brittain at the AT&T bell laboratories,¹³ and with the development of the first integrated circuits by Texas Instruments using silicon and planar fabrication techniques, a giant industry known as semiconductors¹⁴ came to life

A device or single transistor element is simply a junction between two types of semiconductor materials often termed (p & n), formed by diffusing dopants into the silicon substrate. The basic building blocks in microelectronics are the integrated circuits, which are simply interconnected components, such as transistors, resistors, diodes and capacitors fabricated directly onto silicon wafer substrates, called the master-slice. When thousands of these devices are interconnected, using metal wiring such as copper or aluminum, a VLSI circuit is formed.

Figure 2.0.1 is a schematic of an integrated circuit. A VLSI device is a sandwich of many complex layers, each having a unique detailed pattern composed of silicon, inorganic oxides, metal, metal oxides or polymeric materials. The success of an integrated circuit depends on the precise stacking of one layer over the top of another, and the accurate interconnections between the components. Thus, the integrated circuit or chips, which are 1/4 inch squares, are tested and packaged.¹⁵⁻¹⁹

The packaging helps to transform the basic electronic devices into optimized hardware systems that are manufacturable, functional and reliable, without compromising the systems overall performance. Thus, packaging not only helps in linking individual chips with one another, but also enables the chip to communicate with the outside world by



• Figure 2.0.1 Schematics of the devices in an integrated circuit (from ref.²⁰)

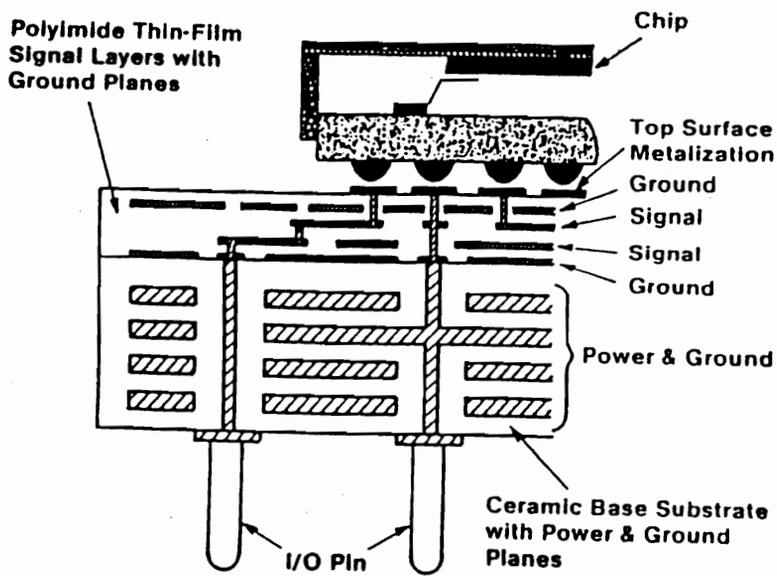


Figure 2.0.2 Schematic of the NEC multichip high-performance package (from ref. ²¹)

providing power, mechanical support, environmental protection and proper heat dissipation. Figure 2.0.2 is a schematic of a high-performance package where many chips are mounted to a multi-level ceramic carrier which is then plugged into a board.

The ever increasing trend towards integrated circuits that are faster, possess higher lead counts, lower power consumption and heat dissipation in multichip modules, places a great demand on high speed "chip to chip" communications, as well as for high speed "package to package" signal and power communications. This is exactly where polymeric material play a current role in the electronics industry, i.e., to achieve this boost in integrated circuit performance.

From the early 1950's, polymers have been a key element in the growth of the semiconductor industry. The progress of polymers from "art" to "science" has led to new synthetic procedures, in addition to a basic understanding of the relationship between molecular structure, mechanical and thermal properties. As the ability to tailor the properties of polymers to one's needs has grown, the industry has been able to supply an ever increasing variety of materials to meet the needs for lightweight, easily handled, low cost polymer materials to fabricate and package logic and memory chips.

This chapter will cover the following topics

- An Overview of Macromolecular Applications in Electronics

- Emerging Trends in Electronics and Their Impact on Plastics

- Critical Polymer Properties for Microelectronic Applications and

- Application of Polymers in the Electronics and Electrical Industry.

- Polyimide Chemistry

- Critical Characteristics of Polyimides for Microelectronic Applications

- Processing of Polyimide Thin Films

- Applications of Polyimide Thin Films

- Future Trends of Polyimides in Microelectronics Industry

2.1 AN OVERVIEW OF MACROMOLECULAR APPLICATIONS IN ELECTRONICS

Phenolic's replaced coated metals for housing and wiring platforms in the beginning of the century, and thus became the first plastic adapted for electronic applications. This was followed by the introduction in the later 1920's of vinyl's and nylons for wire and cable insulation, replacing the original combination of cotton, silk and paper. Other plastics such as ABS and acrylics also found application as insulation in housing.

From the early 1950's, polymers became one of the key elements of growth in the semiconductor industry, with the introduction of two new plastics, the epoxies and the polytetrafluoroethylene (PTFE). Epoxy resins became the material of choice for emerging printed circuit boards, and later for integrated circuit encapsulations, while PTFE began to replace polyethylene and polypropylene as capacitor dielectric's, wire insulators and also in some specialty applications such as microwave circuitry, due to its low moisture absorption and excellent electrical properties.

By the 1970's, polymer materials were used as the basis called the photo-imageable resins for photoresists for making metal patterns. The resins were based on acrylics, thus providing a pathway for high density circuitry, both in the integrated circuit and the printed circuit level. Polyimides have been a more recent and important material for electronics due to their unparalleled temperature stability and excellent electrical properties. Table 2.1.1 shows the year of introduction and typical electronic applications for various plastics.²²

Table 2.1.1 Birth and life of plastics in microelectronics (ref. 22)

Year	Polymer	Application
1909	Phenolic's	Electrical housing, wiring platforms & equipment cases
1927	Polyvinyl chloride	Wire & cable insulation
1938	Polystyrene	Capacitor dielectric's
1942	Polyethylene	Capacitor & wire insulation
1945	ABS & Acrylics Nylon	Wire & cable insulation Circuit boards
1950	Epoxies, Teflon	Encapsulation, adhesives
1957	Polypropylene	Capacitor dielectric's, wire insulation
1964	Polyimide	Dielectric, flexible circuitry
1965	Polyxylenes	Insulation, conformal coatings
1970	Photo-imageable resins	Multilayer circuitry
1975	Polymethyl pentene	Microwave components, cable dielectric's
1980	High temperature thermoplastics, LC polymers	Molded circuitry
1990 & beyond	Conductive polymers & NLO polymers	Active plastic devices

2.2 EMERGING TRENDS IN ELECTRONICS AND THEIR IMPACT ON PLASTICS

The main driving force in electronics packaging and interconnection today are cost, performance and physical space limitation. With the introduction of integrated circuits, a dramatic change has taken place with the rapid increase in the level of electrical functions or components of a chip, resulting in a significant increase in the number of leads/chip.

In order to achieve compact design to meet both miniaturization and speed requirements, fine spacing of leads is required. The delicate nature of such leads and their close spacing imposes severe constraints, such as decreased line width and the increasing number of layers required to keep up with the chip density. This requires materials for packaging and encapsulants with lower thermal coefficient of expansion and lower allowable thermally induced stress. Similarly substrates will need to maintain their dimensional stability, low dielectric constant values, high planarity, etc., to much finer tolerances than in the past.²³ Though some polymers being used presently by the microelectronics industry satisfy these needs, most of them do not. The transformation of polymers from "art" to science has led to newer synthetic procedures and a basic understanding of the relationship between molecular structure and properties. This in turn, has resulted in newer polymer materials waiting to be tested by the microelectronics industry. Figure 2.2.1 shows the trend in packaging.²⁴ The "ideal" property requirements of polymers for the electronic industry is explained in the next section.

2.3 CRITICAL POLYMER PROPERTIES FOR MICROELECTRONIC APPLICATION

Electric applications can be very demanding on materials. Plastics are generally used as insulators and so their electrical properties are critical. However, the materials must also provide good mechanical support, withstand thermal loads and resist

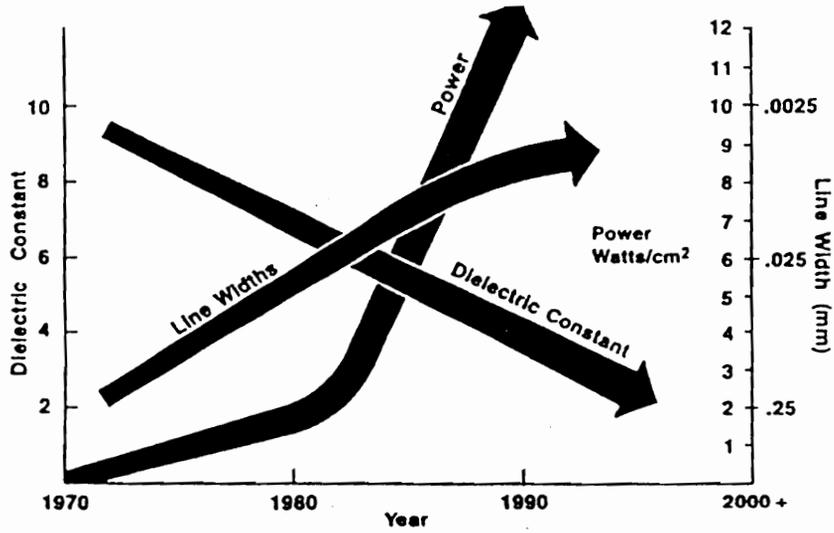


Figure 2.2.1 Trends in electronic packaging (from ref ²⁴)

environmental impact. Hence, all the above properties have to be considered before selecting a polymer for a particular application. Most applications of polymers in electronic packaging have a number of common requirements. These requirements or properties of polymers are as follows²³

2.3.1. Electrical properties

Integrated circuits are very vulnerable to corrosion in the presence of moisture, ionic impurities and electrical fields. Most polymers are not impermeable to moisture, which makes it critical to completely exclude moisture from the packaged device. However, in the presence of moisture, it is very important to minimize the ionic impurity levels, such as cations, which interfere with the electrical performance of the devices while anions such as chlorides and bromides act as catalysts in the promotion of corrosion of copper and aluminum under the influence of moisture.²⁵⁻³⁰

Another important electrical property of polymers to be considered is the dielectric constant. Generally, molecules with more polar groups have higher dielectric constants. Polymers with very low dielectric constants (< 3), such as polyethylene and PTFE, neither routinely meet the combined thermal and mechanical requirements, nor do they possess desirable adhesive characteristics. While most polymers are good electrical insulators in direct current, dielectric losses occur under alternating current conditions. This arises from the fact that molecular dipoles align themselves with the alternating electric field. This property becomes very important, especially at higher temperature where increased molecular motion facilitates the interaction between the dipoles and the external field, thus leading to a thermal runaway.³¹

Thus, ideal polymers are those with low ionic impurity content, low moisture absorption, low dielectric constant, and low dielectric loss at the operational temperature with good adhesion to the substrate is required.

2.3.2. Thermal properties

Both long and short term high temperature stability are important, depending on the type of electronics application. For example, some circuit boards are used at high temperature where long term thermal stability is important, while polyimide interlayer dielectric material is exposed to soldering temperatures of 360°C or less for a limited time. In this example only short term thermal stability is required. Another parameter which changes drastically at or near T_g is the coefficient of thermal expansion (CTE). Typically, the CTE of a polymer above T_g is about three to four times as large as it is below T_g . Clearly, upon thermal cycling a large discrepancy in the CTE's of the materials in a packaged device will lead either to delamination or to stresses on the device. This may result in the cracking of the device, or in the breaking of the electrical connections between the layers of the circuitry, thus rendering the device inoperative.³²⁻³⁴ Therefore, polymers with high glass transition temperatures, stability and low coefficient of thermal expansion are desirable. It should also be pointed out that electronic components also produce large amount of heat, hence the polymer's ability to dissipate heat also becomes very important.

2.3.3. Flammability

Most of the organic polymers are inherently flammable and can generate large amounts of smoke or toxic gases. Polymers with a limited oxygen index of 25 or more are preferred engineering polymers such as polyetherimides and polyether sulfones do meet these requirements.

2.3.4. Chemical / solvent resistance

Solvents and chemicals are generally used in the cleaning, component connection and in the metallization of the plastics. Thus, although requirements for solvent resistance vary with application, polymers with high solvent resistance are generally preferred in thin

film dielectric's area.

2.3.5. Mechanical properties

Since circuit boards made of plastics provide mechanical and environmental protection, properties such as modulus, stiffness or creep resistance becomes important. Hence, polymers with good mechanical properties, such as high modulus, are preferred.

2.3.6. Processibility

Processibility is one of the most important parameters. Polymers, such as epoxies, should have low viscosity's for molding application. Polymers, such as polyimides, which are used as encapsulants or die attach should be highly soluble in solvents such as n-methyl pyrrolidone, so that thin uniform films can be obtained by casting operations.

2.4. APPLICATION OF POLYMERS IN THE FIELD OF ELECTRONICS

The use of polymers in electronics can be grouped into four main categories. They are a) protective gels, b) rigid bulk encapsulants, c) printed circuit board materials, and d) thin films.

2.4.1. Protective gels

Silicones are the materials of choice in this area. These materials are usually crosslinked in nature. The two main advantages of using crosslinked silicones are by simple variation of the backbone structure and chemical composition, one can produce very soft gels, elastomeric compounds or hard solids, and these materials are one of the few systems that exert only minimal on chips, wires etc.³⁵ The disadvantages of these materials are their weak mechanical properties, and devices protected with silicone gels

have to be further protected from the environment by using either ceramic or metal castings.

2.4.2. Rigid bulk encapsulants

The material that is highly preferred as encapsulants are the epoxies, which have replaced earlier encapsulant material, such as silicones, due to the cost of these materials and to the continuously improving performance of the epoxies. The process of choice for applying these resins is via transfer molding. The low molecular weight and hence, the low viscosity of the resins, provides enough time for the liquid resin to surround the delicate IC structures and its wire bonds during transfer molding. The effect of viscosity on the deformation of wire configuration has been reported by Blyler et. al.³⁶ and by Manzione et al.³⁷ Typical transfer molding compositions for encapsulation of electronic devices are mixtures of an epoxy novolac resin, a resin hardener, catalyst, inorganic filler, flame retardants, internal lubricants, carbon black and other additives such as getters to trap ionic impurities, corrosion protection materials and stress releasing agents.^{38,39}

2.4.3. Printed circuit board materials

Rigid composite laminates obtained from paper or glass cloth web and phenolic's or epoxy resins are the materials used for printed circuit boards. Rigid laminates, which are the precursors for the printed circuit boards, are prepared by treating the paper or glass cloth web with a resin, and cutting and stacking the prepregs to give the desired thickness. These are later covered with copper foil, laminated and finally cured. The resin materials are generally thermosets. To form a circuit, a pattern is formed on a resist layer and the laminate is then etched or copper is "plated up" additively. The electrical pathways between layers is formed by drilling and then plating a thin layer of copper on the hole walls. The holes function as points of connection or as mounting holes.

Recently, newer thermosetting materials, such as the poly(cyanurates)⁴⁰ and poly

(benzocyclobutanes), are being investigated for PWB's.^{41,42} Three dimensional interconnects have also been prepared through several direct molding processes using various thermoplastic materials, such as Udel[®] polysulfone, Victrex[®] poly(ether sulfone), Radel[®] poly(aryl sulfone), poly(etherimides), poly(phenylene sulfides), or poly(phenylene oxides), and also fluorinated ethylene propylene copolymers.⁴³ An excellent review of the recent advances in thermoplastics for electronic applications is available.²⁴

2.4.4. Thin films

Due to the success of polyimides in other fields of electronics, they became the first choice for thin film dielectric material in interconnections. An overview of polyimide chemistry, processing and application in the field of microelectronics will be reviewed in the next chapter.

2.5 POLYIMIDE CHEMISTRY

Polyimides are one of the best known heterocyclic polymers with remarkable thermal stability. These materials are characterized by the presence of the phthalimide structure in the backbone.

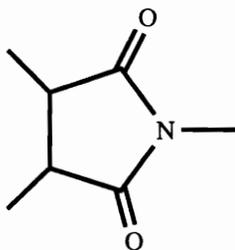


Figure 2.5.1 Chemical structure of imide linkage

The earliest attempts to synthesize polyimides are believed to have occurred around 1908.⁴⁴ Polyimides have been used in the electronics industry for some time as polymer insulation

materials, because of their excellent electrical and mechanical properties at elevated temperatures.⁴⁵ Although there are other polymers whose thermal stability compares favorably with polyimides, these polymers are generally insoluble, intractable and lack processability. One of the first commercially available resins for electrical insulation marketed in the 1960's was pyre-ML by DuPont.⁴⁶ This resin was evaluated as a spin castable thin film dielectric in the early 1970's, and as a planar insulating material in other branches of electronics. The same material in the form of cured film was marketed by DuPont under the trade name of "Kapton". Work on the use of polyimides as a multilevel interconnect dielectric was established by Hitachi in 1973.^{10,47} Thus, the application of polyimides in electronics has been mainly in the passivation and protection areas. But in recent years it has been extended for use as an intermetal dielectric in IC's or thin film electronic packaging. Recent advances in photo imageable polyimides and polyimide-poly(dimethyl siloxane) block copolymers has further accelerated the use of polyimides for electronics application.^{48,49} Several good review articles and books are available on polyimide chemistry and applications.⁵⁰⁻⁵⁴

The literature review, though not exhaustive, is intended to serve as a background for the experimental section that follows. The research in this dissertation and the literature review cover several areas in polyimide chemistry. The first section discusses common synthetic methods used to make polyimides. The second section discusses necessary properties for electronic applications. The third section focuses on the processing and use of polyimides in electronics. Finally, this chapter reviews the various methodologies used to synthesize polyimide foams, their properties and applications.

2.5.1. Polyimide Synthesis

The classical method of synthesizing polyimides involves a two step process, wherein the first step involves the polycondensation reaction of a dianhydride and a

diamine in a polar aprotic solvent. This results in the formation of the poly(amic acid), which in the second step, is cyclodehydrated either by thermal or chemical means to form the polyimide.⁵⁵⁻⁶⁰ Figure 2.5.2 depicts the classical two step synthetic procedure used for polyimide synthesis.

2.5.2. Poly(amic acid) Synthesis

The synthesis of the poly(amic acid) involves the nucleophilic substitution of one of the anhydride carbonyl carbons by an amine functionality. The poly(amic acid) synthesis has been shown to be an equilibration reaction proceeding via the mechanism shown in Figure 2.5.3.^{61,62} The nucleophilic attack of the amine on the anhydride carbonyl results in the formation of an amide bond and a free carboxylic acid group. Polar aprotic solvents, such as *n*-methyl pyrrolidone (NMP) or dimethyl acetamide (DMAC), are used in the synthesis of poly(amic acid) to form strong hydrogen bonds with the carbonyl groups, and thus, solvate the carbonyl group and drive the reaction towards the polymer function.

Molecular weight and molecular weight distribution are dramatically affected by the equilibration of the poly(amic acid). The equilibration reaction was clearly demonstrated by Cotts and coworkers, who combined two poly(amic acids) of different molecular weights and followed the course of reaction using gel permeation chromatography technique (GPC). Initial GPC traces showed two peaks, but over time, the peaks were observed to merge, resulting in one peak with a gaussian or most probable molecular weight distribution.⁶³

The equilibration reaction was initially thought to occur either by hydrolysis^{64,65} or through transamidation.⁶⁶ Recently, it has been shown that the equilibration reaction occurs through the degradation of the poly(amic acid), generating anhydride and amine end groups.^{67,68} The cleaved poly(amic acid) was observed to recombine in a statistical fashion, producing the most probable molecular weight distribution. These results are

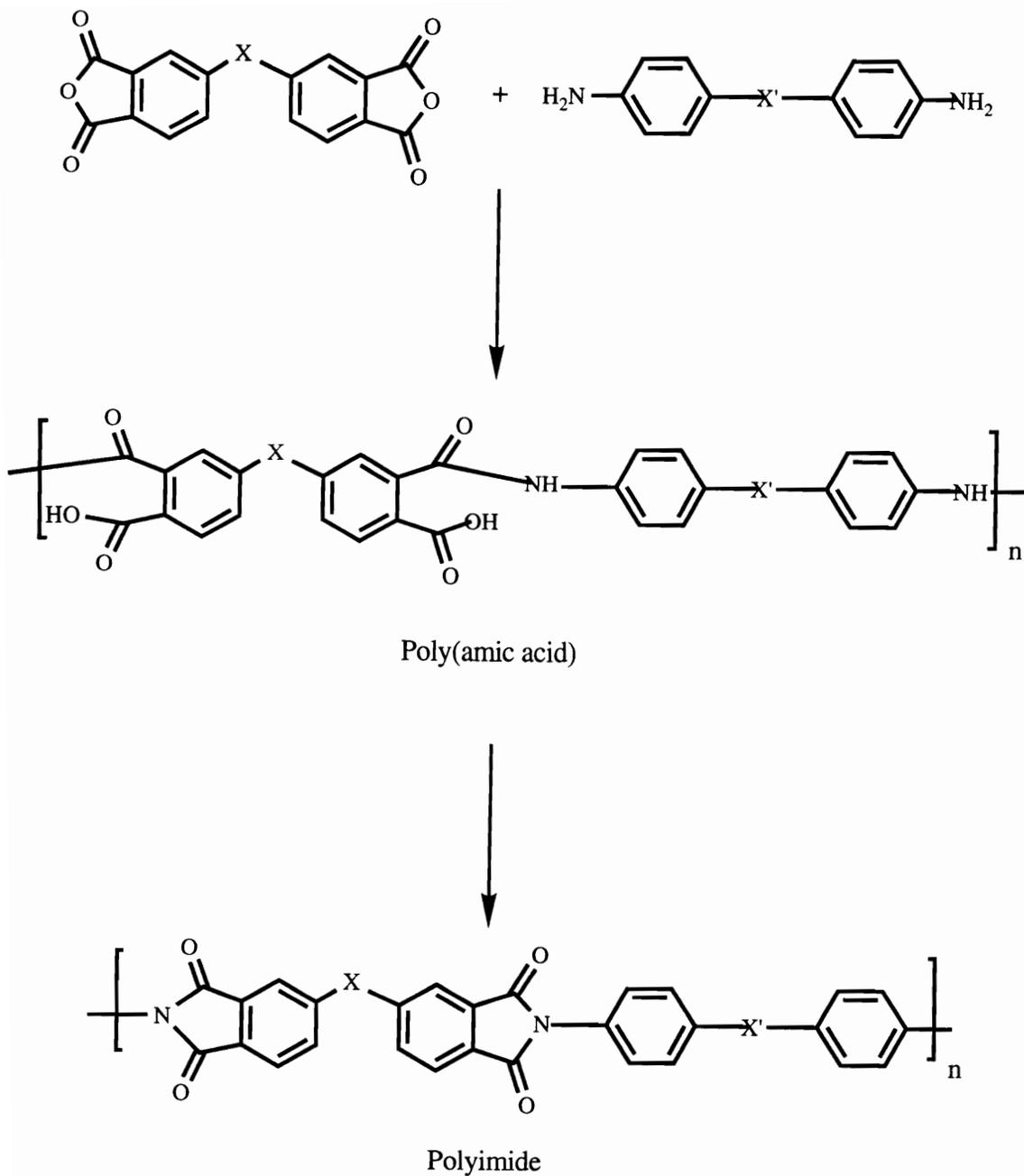


Figure 2.5.2. Classical two step synthesis of polyimides

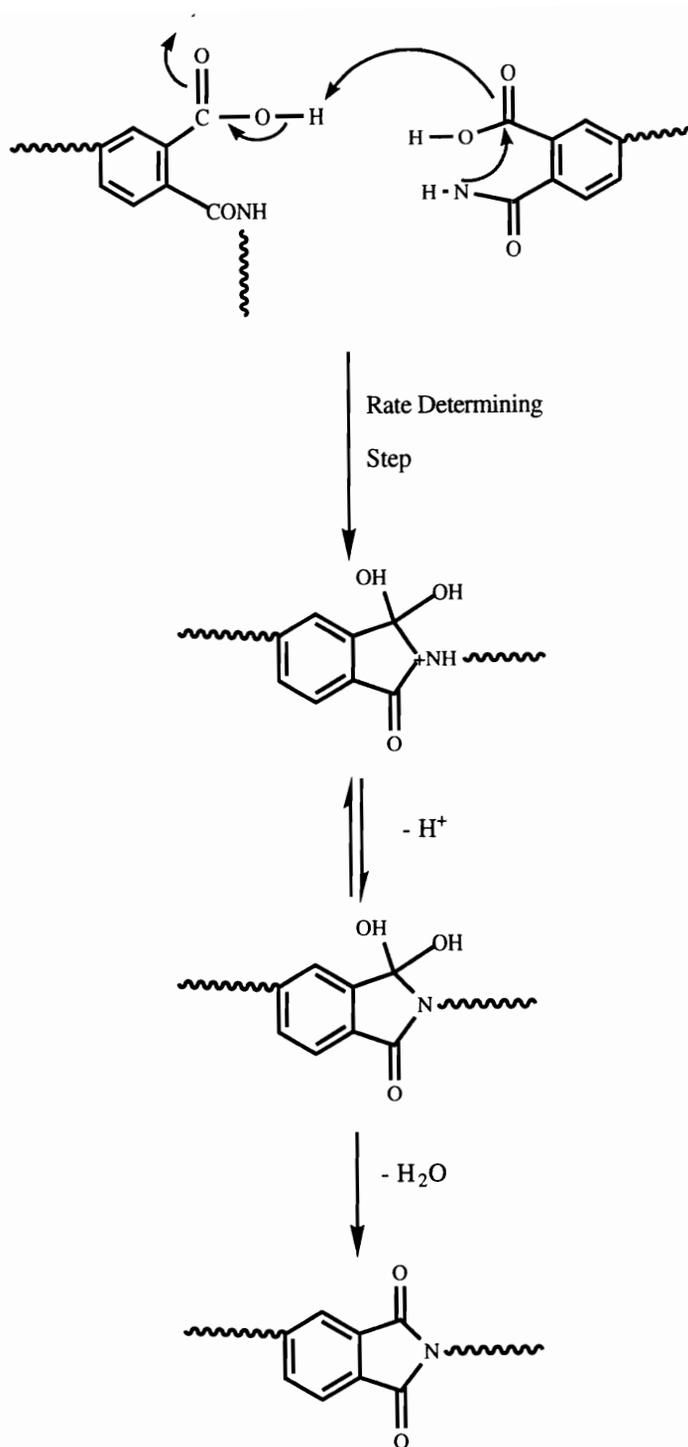


Figure 2.5.3 Mechanism of Imidization of Poly(amic acids) in solution (from ref.^{61,62})

consistent with the other results. For example an increase in the reaction temperature or a decrease in the solid content of the reaction was observed to decrease molecular weight. Presence of excess dianhydride or diamine monomers was also observed to decrease the poly(amic acid) solutions molecular weight.⁵¹

In general, the synthesis of poly(amic acid) is performed under anhydrous conditions. The monomers and solvents must be carefully dried, as the presence of water in the reaction mixture results in the hydrolysis of the anhydride, effectively limiting the molecular weight of the poly(amic acid).

2.5.3. Bulk Imidization

Conversion of the poly(amic acid) to the corresponding polyimide can be performed by either bulk, solution, or chemical imidization methods. Bulk imidization is usually conducted by heating the poly(amic acid) in stages close to, or above, the ultimate T_g of the polyimide in order to achieve complete cyclization and solvent removal. Bulk imidization is the most common method, which often produce insoluble polyimides, possibly due to high temperature side reactions such as crosslinking.^{66,69-71}

2.5.4. Solution Imidization

Poly(amic acids) can be converted into completely cyclized polyimides by heating the solution of the poly(amic acid) to about 150 to 180°C in the presence of an azeotroping agent, such as o-dichlorobenzene (ODCB), xylene or cyclohexyl pyrrolidone (CHP).^{72,73} Conversion of poly(amic acids) to polyimide in solution is achieved at a lower temperature, due to greater mobility of the polymer in solution. The use of an azeotroping agent also ensures the removal of water generated during the reaction, thus driving the reaction forward. Complete imidization is temperature dependent, but usually achieved within 16 to 20 hours, under N₂ atmosphere.

Polyimides have also been formed in one step at 180 to 220°C in solvents such as m-cresol.⁷⁴

The solution imidization process was investigated by Kim and coworkers and was found to proceed by an auto acid catalyzed second order kinetics.⁷⁵ The attack of the amide nitrogen on the carbonyl to afford the imide ring has been shown to be the rate determining step for this reaction. Polyimides obtained from solution imidization have been observed to be more soluble, and lighter in color when compared to analogous bulk imidized polyimides due to fewer, if any, side reactions.

2.5.5. Chemical Imidization

The cyclization of the poly(amic acids) to the corresponding polyimides can also be achieved at ambient temperature using chemical imidization methods.^{76,77} The reaction is achieved by treating the poly(amic acid) with a dehydrating agent such as an aliphatic carboxylic dianhydride, and a basic catalyst such as a tertiary amine. The mechanism for the conversion of the poly(amic acid) to the polyimide is shown in Figure 2.5.4.⁵¹

The first step in the dehydration is the formation of a mixed anhydride. The tertiary amine may accelerate this process by forming a complex with the anhydride. The nucleophilic strength of the amide group may also be increased under the influence of the base (R_3N with CH_3COO^- or the carboxylate ion). In the final stage, the water produced as a result of cyclization may be captured by excess anhydride.

In 1974, Vinogradova et al. reported the chemical cyclization of a poly(amic acid) solution in DMAc directly to a polyimide.⁷⁸ They had achieved this conversion by the addition of acetic anhydride / pyridine mixture to the poly(amic acid) solutions in DMAc. The optimum ratio of acetic anhydride / pyridine (4:3.5) per poly(amic acid) basic molecule and the choice of base had a significant effect on the conversion process. The use of higher basicity trialkyl amines produced polyimides in higher yields and of higher molecular

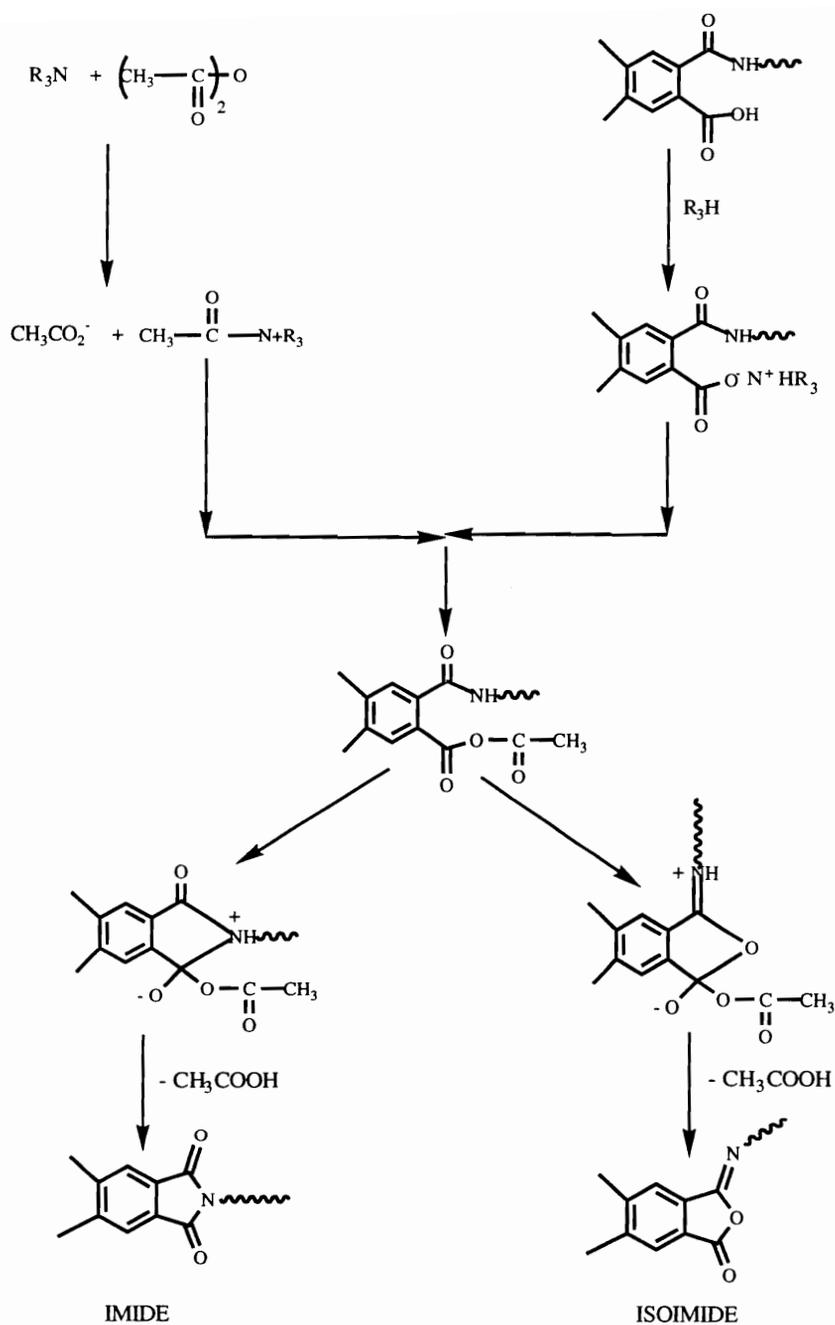


Figure 2.5.4 Mechanism For the conversion of Poly(amic acid) to Polyimide via chemical imidization technique (from ref.⁵¹)

weight than the less basic tertiary amines.

The major disadvantages of chemical imidization at room temperature are incomplete conversion of poly(amic acid) and isoimide formations⁷⁹⁻⁸¹ which is outlined in Figure 2.5.4. Polyimides obtained from chemical conversion have been observed to have lower mechanical properties than thermally imidized samples, due to the existence of these unstable linkages. The isoimides have been observed to convert the imide linkages on aging at 100°C for several days, or at much higher temperatures for a few hours.

2.5.6. Miscellaneous Polyimide Synthetic Methods

2.5.6.1. Polyimides via poly (amic alkyl ester) route

Poly(amic alkyl ester)s are another approach to improve the processability of polyimides. The derivatization of the carboxylic acid moieties along the poly(amic acid) backbone in the form of the alkyl ester groups provides increased synthetic flexibility, as well as improved hydrolytic stability relative to the traditional poly(amic acid) precursor route. The poly(amic alkyl ester)s also provide the flexibility of widely varying the imidization temperature via the choice of the alkyl ester group. Thus, when lower imidization temperatures associated with poly(amic acid) are required, the amic ester approach is still applicable by the use of t-butyl ester, while higher imidization temperatures are employed when ethyl or propyl derivatives are chosen. The poly(amic alkyl ester)s have been observed to have much higher solubility in polar aprotic solvent, in comparison to the corresponding polyimides. This approach is desirable for high solid content formulations with significantly improved planarization characteristics, which are highly desirable for electronics applications. Hence poly(amic alkyl ester)s are highly versatile polyimide precursors for improved dielectric coatings.⁸²

Poly(amic alkyl ester)s are usually synthesized by the incremental addition of the

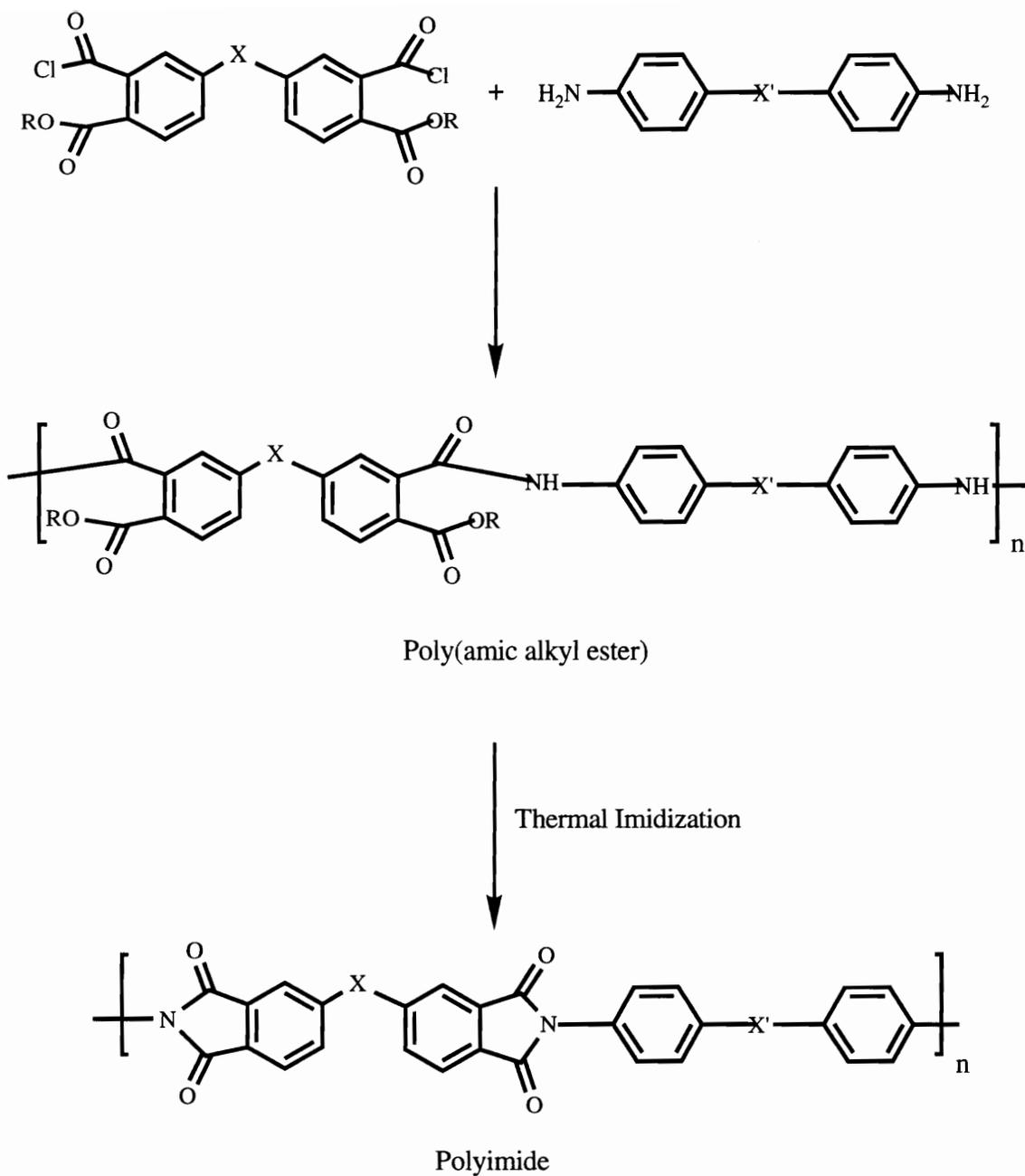


Figure 2.5.5. Synthesis of Polyimide via poly(amic alkyl ester)s (from ref.⁸³)

diethyl ester diacyl chloride of PMDA in dry THF to a solution of diamine in NMP containing pyridine as the acid acceptor. The reaction scheme for the synthesis of the poly(amic alkyl ester)s is provided in Figure 2.5.5.⁸³

In the synthesis of the precursor poly(amic alkyl ester) polymer, the nucleophilic substitution reaction on the diacid chloride carbonyl by the diamine may occur in the meta or para position. Generally the resulting poly(amic alkyl ester) is a statistical copolymer containing 50% meta and 50% para linkages. Volkson et. al. have recently developed a synthetic procedure that can create poly(amic alkyl ester)s with all para or all meta connections along the chain by the use of the appropriate diethyl ester diacyl chloride isomer (i.e. meta or para) of PMDA and the required diamine.⁸⁴ This has led them to investigate the effect of the isomeric structures on the ring closing imidization reaction.⁸⁵

Protection of the free acid groups of the poly(amic acids) by the formation of the diethylamides, instead of the alkyl esters, have also been suggested as a means of increasing their stability.⁸⁶

2.5.6.2. Ester-acid route to polyimides

The synthesis of polyimides by the ester-acid route is shown in Figure 2.5.6. This method involves the combination of an aromatic diamine with an aromatic diester diacid in a combination of a polar aprotic solvent, such as NMP, and an azeotrope such as ortho-dichloro benzene (ODCB). The synthesis of polyimides is achieved at 180°C in about 10 to 24 hours.

The main advantage of the ester-acid route is the conversion of the water sensitive anhydride group to a water insensitive ester acid group. Thus, small amounts of moisture in the reaction mixture have been observed to have little or no effect on polymerization.⁸⁷ In addition, the low molecular weight imide precursor can wet both glass and ceramic fibers easily.

2.5.6.3 Anhydride - isocyanate route to polyimides

Polyimides can be formed from aromatic tetra acids and their dianhydrides by condensation with diisocyanates. The final chemical structure obtained via this method is thought to be identical to structures obtained through classical polyimide chemistry, although the intermediates have been observed to be different.⁸⁸ Hurd and Prapar have proposed the reaction between the anhydride and an isocyanate reaction to proceed partially through the formation of a seven membered ring followed by decomposition of the cyclic intermediates to evolve CO₂ and water thus yielding the imide structure.⁸⁸ The reaction scheme for the synthesis of polyimides via the isocyanate route is shown in Figure 2.5.7.⁸⁹ Several key reaction conditions have to be satisfied in order to reproducibly synthesize linear high molecular weight polyimides. Small amounts of water are required for this reaction to proceed. The use of small amounts of tetraacid with the dianhydride effectively includes the required amount of water for the reaction to proceed, and also helps in overcoming the solubility problems associated with this synthetic method. High quality polyimides are obtained when (a) the acid anhydride ratio is between 1:1 and 1:4 (b) tertiary amines are as used catalyst (c) solid diisocyanate is added to the anhydride solution and (d) the reaction is performed between 10 and 100°C, even though the evolution of theoretical quantities of CO₂ do not occur until temperatures of 200°C is reached.

2.5.6.4. Transimidization

Transimidization was first reported by Spring and Woods using phthalimide and methylamine.⁹⁰ Imai adopted this transimidization reaction to make high molecular weight polyimides by reacting N,N-bis(ethoxy carbonyl) pyromellitimide and an aromatic diamine for seven days at ambient temperature, and later heating the intermediate to 240°C to obtain the polyimide.⁹¹ Extensive work has been done in this field by Takekoshi and co-workers, which has resulted in the synthesis of various poly(ether-imides).⁹²⁻⁹⁴ Figure 2.5.8 shows

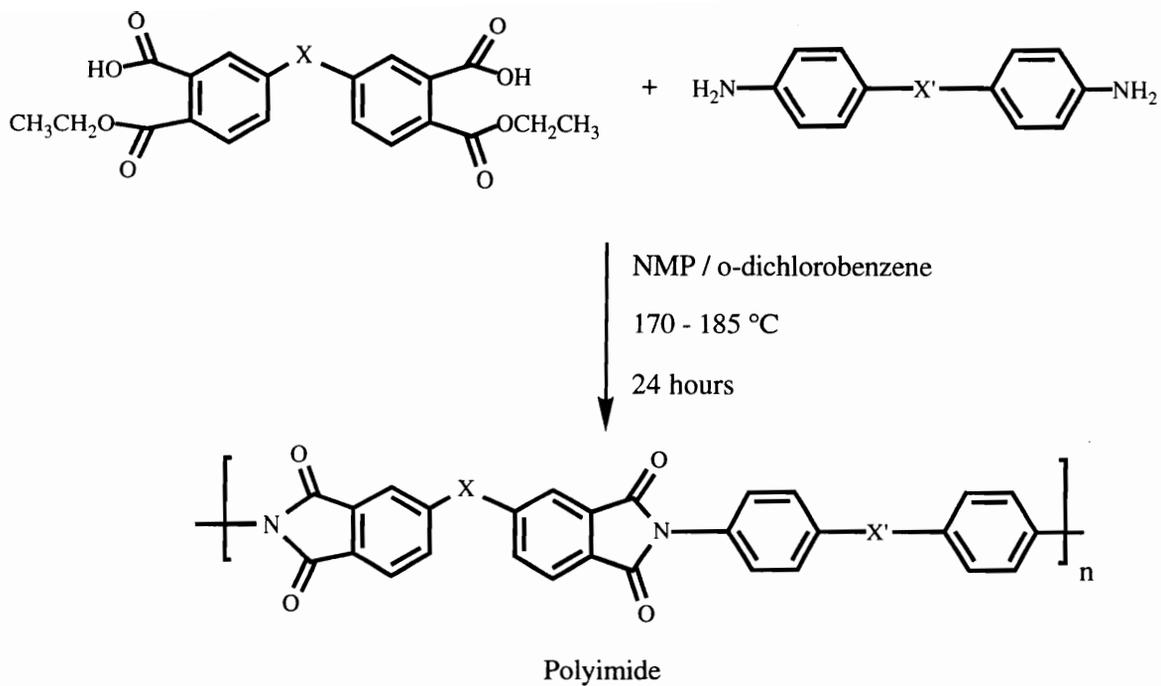


Figure 2.5.6 Synthesis of polyimide via ester acid intermediates

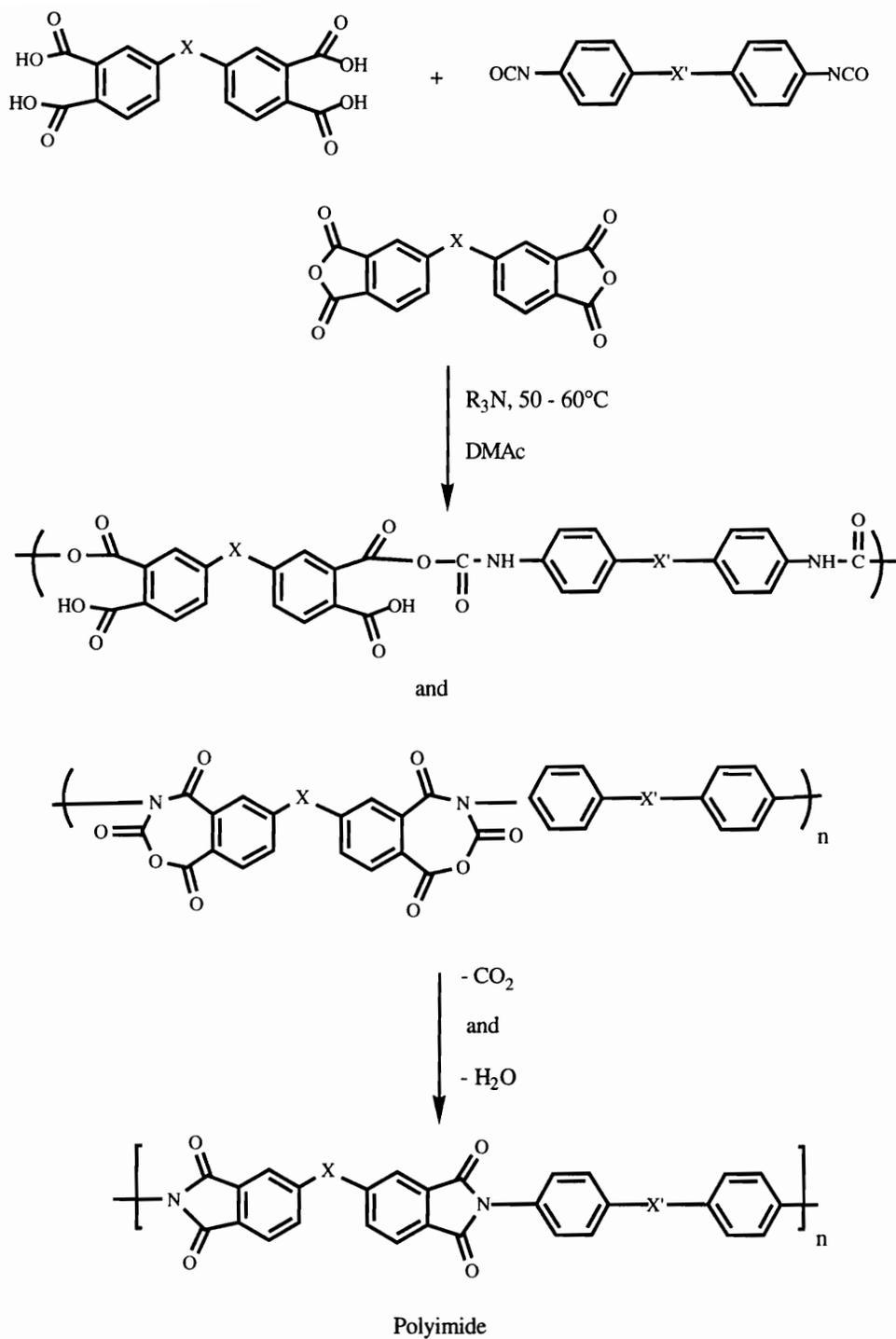


Figure 2.5.7 Synthesis of polyimides via the diisocyanate route (from ref. ⁸⁹)

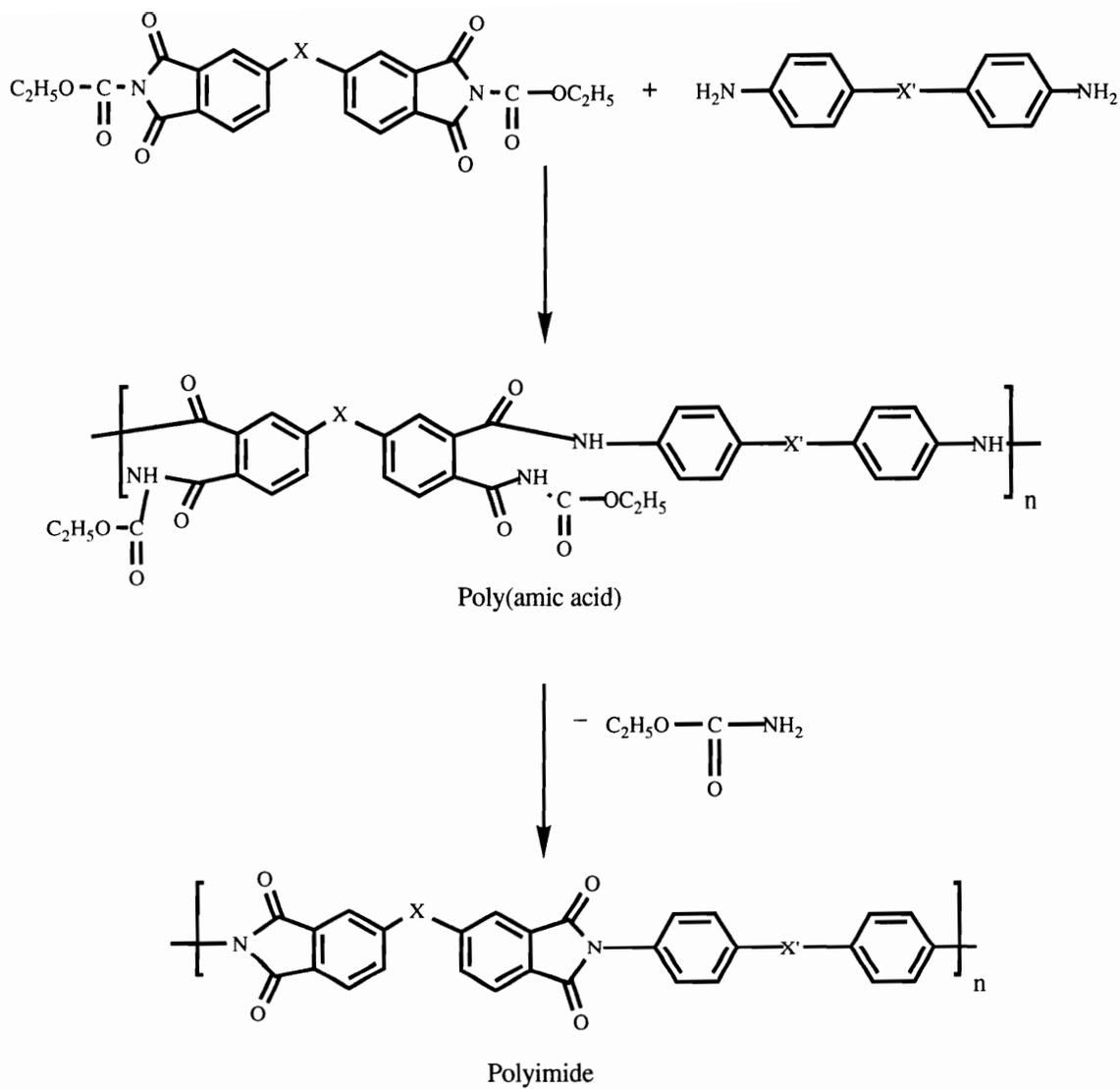


Figure 2.5.8. Synthesis of polyimide via trans imidization (from ref.⁹¹)

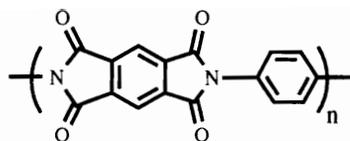
the reaction scheme for the synthesis of polyimides via this method. Rogers et. al. have recently extended this approach for the synthesis of polyimide - siloxane block copolymers.

2.6. PROPERTIES OF POLYIMIDES FOR MICROELECTRONIC APPLICATIONS

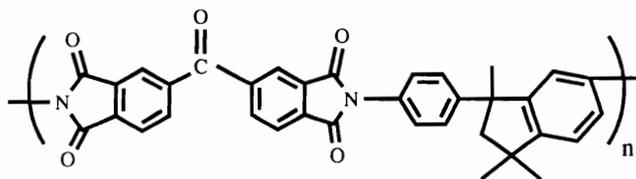
Polyimides are recognized as one of the most thermally stable organic polymers. Well developed synthesis and solution processing from the poly(amic acid) stage, which produces good step coverage for the topological substrates, has made polyimides an essential and useful material for the manufacture of semiconductor devices. Applications have been recently expanded to other electronic devices, such as multi chip packaging, liquid crystal displays, etc.^{95,96} Two types of polyimides are used for electronic applications, namely non-photosensitive and photosensitive systems. The non-photosensitive polyimides include (a) conventional polyimides, (b) polyimides containing isoindoloquinazoline and (c) polyimide - siloxane block and random copolymers. These chemical structures are shown in Figure 2.6.1.^{97,98} In the case of the photosensitive polyimide, the photosensitivity of the polyimide structure is introduced either via covalent bonding or through an ionic bonding method. In the former, the photosensitive group is incorporated into the polyamic acid through covalent bonds by reacting photosensitive monomers,⁹⁹ while in the latter, a tertiary amine having a photosensitive group is reacted to form a salt with the carboxyl group of the poly(amic acid).¹⁰⁰ These are shown in Figure 2.6.2.

In order to be used in electronic devices for various applications polyimides must satisfy some basic properties, such as preserving the electrical function of the device. A polyimide that is to be used as an inter-layer dielectric or protection layer must satisfy the various properties shown in Table 2.6.1.¹⁰¹

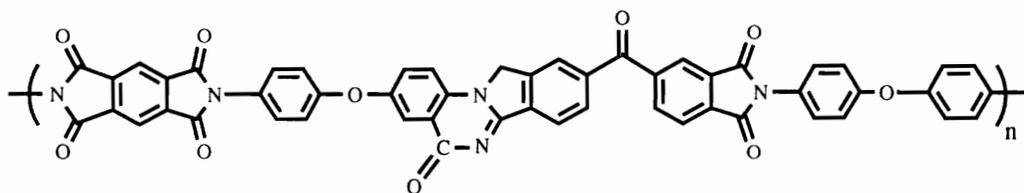
What follows are the fundamental properties of polyimides discussed from the point



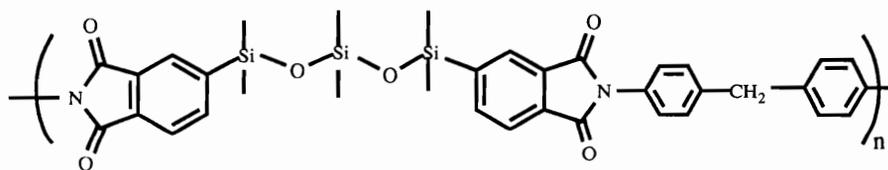
Conventional Polyimide
Trade Name Dupont Kapton



Conventional Polyimide
CIBA GIEGY XU - 218



Polyimide Coating
Hitachi PIQ Resin



Polyimide - Siloxane Copolymer

Figure 2.6.1. Commercially available non-photosensitive polyimides used for microelectronics application (from ref. ⁹⁸)

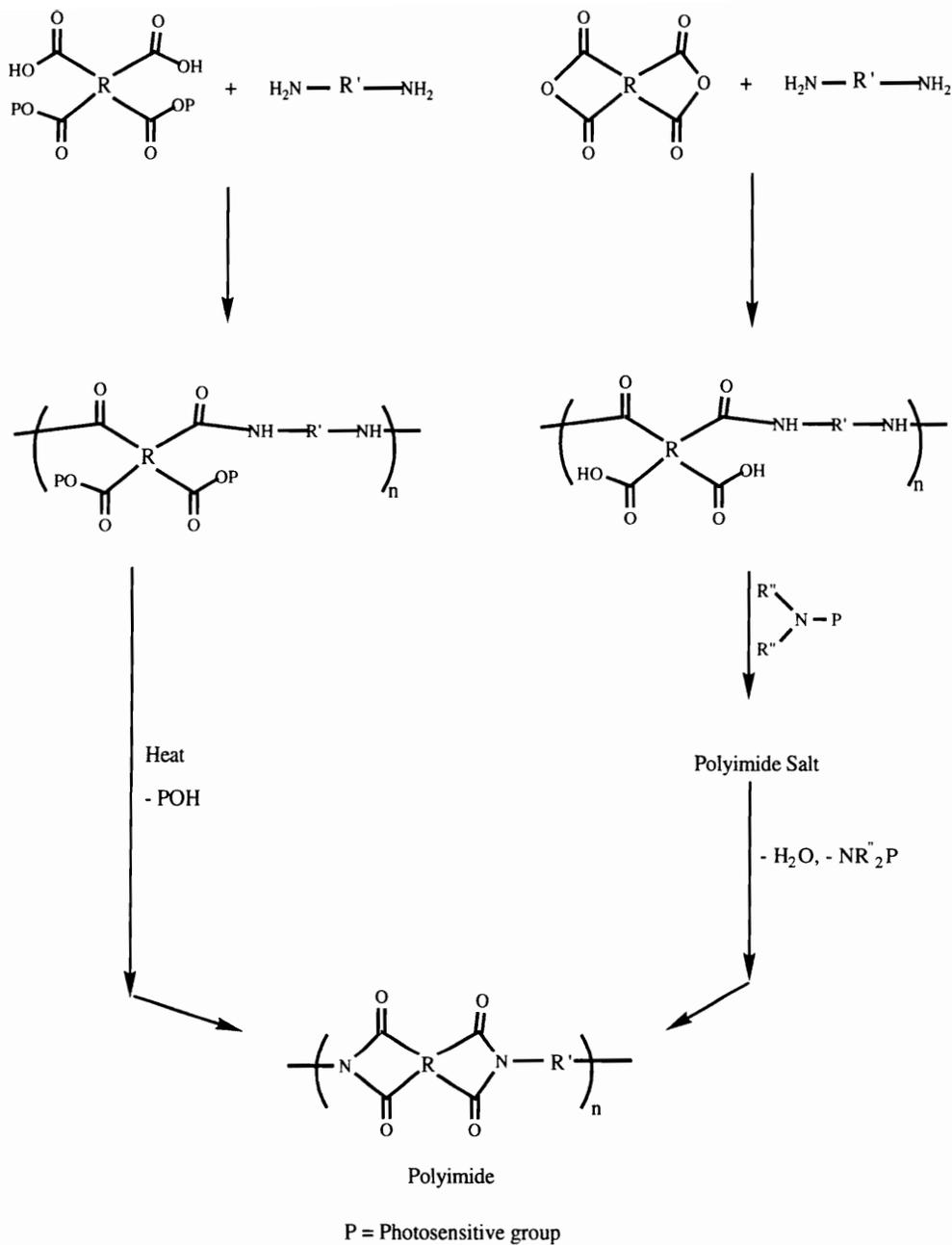


Figure 2.6.2 Chemical structure of photosensitive polyimide a) covalent bonding type and b) ionic type (from ref. ^{99,100})

Table 2.6.1 Required properties for an insulating layer in semiconductor devices (from ref. 101)

Item	Passivation Film	Interlayer Insulating Film
Device Characteristics	1) No effect on the characteristics during film formation	
	2) Low temperature formation (< 400 - 450°C)	
	3) No deterioration of Al surface	
	4) Low charge density	
		5) Low dielectric constant
		6) High electrical resistivity
Increase of circuit density		1) Planar surface (step coverage)
		2) Fine patterning
Reliability	1) Low defect density	
	2) High heat resistance	
	3) High mechanical strength and good chemical resistance	
	4) Good adhesion	
	5) Low water permeability, absorption and low mobile ions	
	8) Blocking ability of outside contamination	
	9) Electrical stability	

of view of microelectronics applications.

2.6.1. Heat resistance

Polyimides for electronic applications must be able to withstand a large number of heat treatment processes. Even if the high temperature steps are minimized, there are a number of other essential operations that need to be conducted at temperatures ranging from 200 to 400°C. These include sealing, packaging, die bonding, wirebonding and soldering. This requires the glass transition temperature of the polyimide to be higher than any of the above processing temperatures in order to avoid structural deformation in the interconnect device. The glass transition temperature of polyimides are highly dependent upon chemical structure, thermal history and molecular weight of the polymer. Table 2.6.2. reports the glass transition temperature of a number of structurally different polyimides. In almost all cases, efforts to improve polymer processability through introduction of chain flexibility have led to the detrimental effect of lowering the T_g or upper use temperature of the polymer. Excellent reviews are available for additional information on the structure/ T_g relationships of polyimides.^{102,103}

Organic polymers, such as polyimides, are expected to meet the same requirements imposed on inorganic materials, in order to be used as a dielectric layer. For example, the polyimides must have minimal out gassing of residual solvent or moisture. Thermal stability up to 400°C without volatile by-products is necessary for the subsequent metal sinter step, required in integrated circuit manufacture. The thermal stability of aromatic polyimides, as judged by thermogravimetric analysis, is outstanding. Polyimide films remain briefly stable to over 500°C under vacuum or air atmosphere.¹⁰⁴ Above this temperature, there is a sharp increase in the rate of weight loss.

Polyimide films for electronic applications are usually formed from poly(amic acid). The poly(amic acid) is coated on the substrate, (usually a wafer) and heated to temperatures

GLASS TRANSITION TEMPERATURE

(°C)

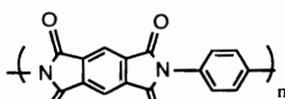
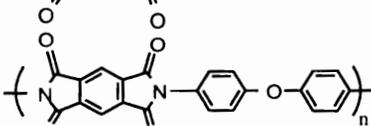
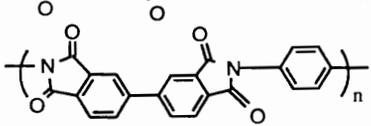
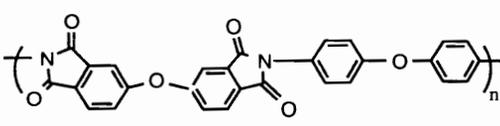
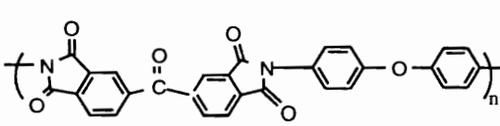
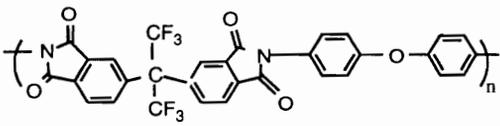
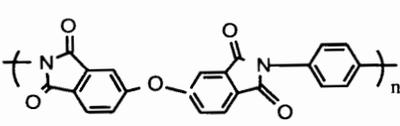
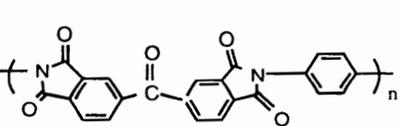
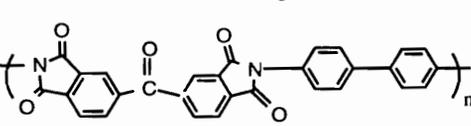
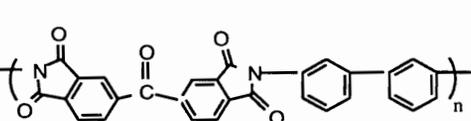
	-
	399
	390
	270
	279
	222
	342
	300
	290
	264

Table 2.6.2 Effect of structure on glass transition temperature of polyimides (from ref. 102,103)

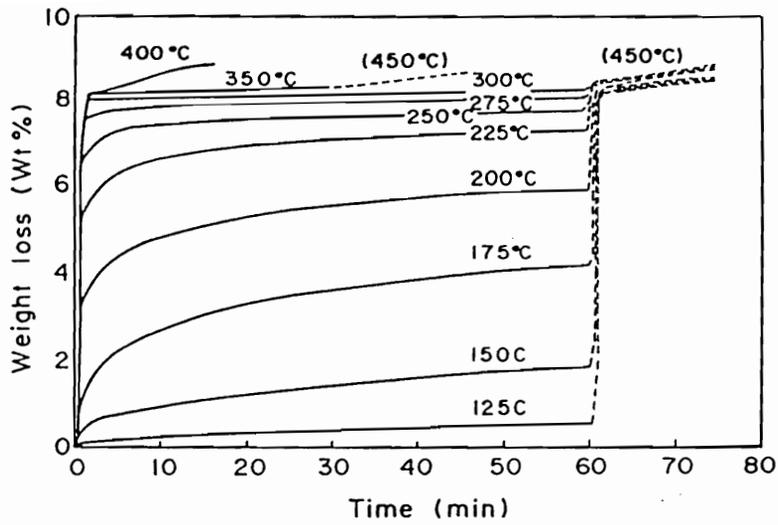


Figure 2.6.3 Weight loss of water during imidization reaction for PMDA/ODA based polyimide (from ref. ¹⁰⁵)

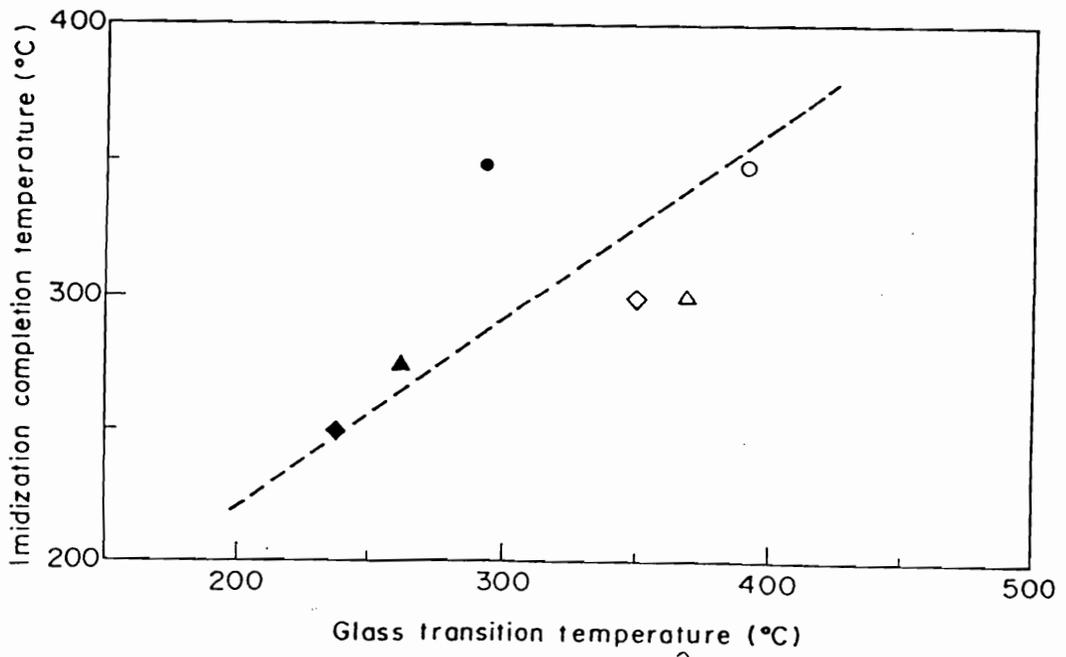


Figure 2.6.4 Correlation between fully imidized temperature and glass transition temperature (from ref. ¹⁰⁵)

between 200 to 400°C to produce polyimide films. An incomplete imidization reaction can cause deterioration of both chemical and physical properties. Figure 2.6.3. shows the weight loss of water generated during the imidization reaction at a specified temperature.¹⁰⁵

The imidization reaction has been observed to be substantially affected by temperature, rather than time. Figure 2.6.4.¹⁰⁵ also shows the relationship between the polyimide's T_g and the imidization temperature has been observed to be linear. Incomplete imidization also would result in film porosity, due to evolution of water at the servicing and processing temperature, which could cause premature failure of the chip. Thus, polyimides produced from poly(amic acids) having a high T_g must be cured at high temperature, usually 20 to 30°C higher than the T_g .

2.6.2. Coefficient of thermal expansion

Thermal stress originates in a mismatch of the coefficient of thermal expansion of the polyimide film and substrate. The thermal stress is expressed by the following formula

$$Z_T = E_f (a_f - a_s) (T_b - T) / (1 - \nu_f)$$

$$Z_T = \text{thermal stress at temperature } T$$

E_f and ν_f are the Young's modulus and Poisson's ratio of the Polyimide film

T_b = temperature to which the film was cured and

a_f and a_s are the thermal expansion coefficient for substrate and film.

When the polyimide is coated on a substrate and $a_f > a_s$, thermal stress remains in the film, which often causes the film to crack and peel of the substrate. Numata has investigated the relationship of molecular structure to the coefficient of thermal expansion for a series of polyimides using a thermal mechanical analyzer.³² These results are provided in Table 2.6.3. Thermal expansion coefficient values for polyimides range from $3 * 10^{-6}$ to $15 * 10^{-6}K^{-1}$ and polyimides whose molecular structure are rigid or rodlike have been observed to have lower thermal expansion coefficient values. Thus, it is

Thermal Expansion Coefficient of Polyimide* ($\times 10^{-3} \text{ K}^{-1}$)

	(1)	(2)	(3)
(A) 	—	0.26	2.10
(B) 	3.20	4.00	2.94
(C) 	—	3.19	3.95
(D) 	0.04	0.58	2.59
(E) 	3.48	4.00	3.95
(F) 	1.61	—	—
(G) 	0.59	0.54	2.17
(H) 	0.20	0.56	1.54
(I) 	1.37	4.64	4.91
(J) 	0.56	0.59	1.83
(K) 	—	1.72	—
(L) 	1.58	1.13	1.60
(M) 	2.16	4.56	4.28
(N) 	4.15	4.61	5.24
(O) 	4.57	4.18	4.50
(P) 	5.76	4.85	5.36
(Q) 	—	1.00	2.61
(R) 	5.33	5.32	5.43
(S) 	5.01	5.69	5.39

Table 2.6.3 Effect of structure on coefficient of thermal expansion of polyimides (from ref.³²)

Table 2.6.4 Summary of electrical properties of candidate interconnection dielectric materials (from ref.¹⁰⁷⁻¹¹⁰)

Material	Frequency (KHZ)	Dielectric constant	Dissipative factor	Volume resistivity	Breakdown voltage (Mv/cm)
----------	-----------------	---------------------	--------------------	--------------------	---------------------------

Hitachi PIQ	1	3.4 - 3.8	0.002		
or DuPont PI2525	1000	3.8			3.2
Silicon PI	1	3.0 - 3.5			
Acetylene terminated PI	1	2.9 - 3.4	0.002		
BCB	1	2.6	0.00045		
	10 - 1000	2.66	0.003-0.0001		2.5 - 4.0
Si		11.7 - 12			
SiO ₂		3.5 - 4.0			
Si ₃ N ₄		7 - 10			
Al ₂ O ₃		7 - 9			
Polyquinoline	10 ⁶	2.5 - 2.6			
Parylene N	0.06	2.65	0.00035 - 0.0004	10 ¹⁷	2.76
	1	2.65			
Parylene D	0.06	2.64		2 * 10 ¹⁶	2.17
	1	2.82			

possible to select a polyimide whose thermal expansion coefficient matches those of metals or inorganic materials used in the fabrication of electronic devices.

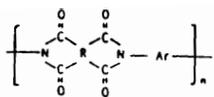
2.6.3. Dielectric constant

Dielectric constant is defined as the ratio of measured capacitance of a capacitor between a given dielectric material and that of the same capacitor using a vacuum dielectric. For microelectronics applications, low dielectric constant is a requirement to minimize interconnect capacitance, resistivity losses, propagation delay and crosstalk between signal lines.¹⁰⁶ These help in allowing circuits to be run with a lower power input. Table 2.6.4 summarizes the electrical properties of candidate interconnection dielectric materials.¹⁰⁷⁻¹¹⁰

Low dielectric constants are exhibited by materials that have low stress, high polymer chain rigidity and low polarity polymers. St. Clair et. al. have studied the structure to property relationships of highly insulative, low dielectric constant polyimides¹¹¹ and their results are provided in Table 2.6.5. Commercially available polyimides have a dielectric constant ranging from 3.2 to 4.0. These values depend not only on the frequency at which the measurements are made, but also on the amount of moisture uptake of the polyimide. In general, the polymer dielectric constant has been observed to increase linearly from 3.1 to 4.1 as humidity increases from 0 to 100%.^{106,112} But polyimide dielectric constant has been observed to decrease with increasing frequency. It was suggested that polymer conformations become restricted and cannot respond to the alternating field at sufficiently high frequencies.¹¹³

2.6.4. Dissipative factor (D)

Dissipative factor (D) is defined as the ratio of the current in the resistive component to the current in the capacitive component.



POLYMER ^a	DIANHYDRIDE R	DIAMINE Ar	DIELECTRIC CONSTANT at 10 GHz ^b
PHDA + 4,4'-ODA (KAPTON®)			3.22(3.25) ^c
PHDA + 3,3'-ODA			2.84
BTDA + 4,4'-ODA			3.15
BTDA + 3,3'-ODA			3.09
ODPA + 4,4'-ODA			3.07
ODPA + 3,3'-ODA			2.99
HQDEA + 4,4'-ODA			3.02
HQDEA + 3,3'-ODA			2.88
BOSDA + 4,4'-ODA			2.97
BOSDA + 3,3'-ODA			2.95
6FDA + 4,4'-ODA			2.79
6FDA + 3,3'-ODA			2.73

^a Films were desiccated prior to testing

^b Measurements were run at room temperature and approximately 25% RH

^c Value in parentheses was obtained on commercial Kapton® H film

Table 2.6.5 Effect of structure on the dielectric constant of polyimides (from ref.¹¹¹)

$D = \tan d = PF / 1 - (PF)^2$, where PF = pair factor

d = dielectric loss angle

D is a measure of the electrical energy loss in the material and low dissipation factors are required for polymers to be used in microelectronics. The dissipation factor (D) has been observed to increase with increase in humidity,^{12,114} and decrease with percent imidization. It also increases as a function of the degradation of the polyimide.^{112,115}

2.6.5. Dielectric breakdown strength

The breakdown strength measures the ability of the material to withstand voltage without breakdown on the passage of considerable volts of current. It is defined as the minimum voltage before breakdown occurs and it depends on structure, impurities and humidity. In general, for semiconductor applications a breakdown voltage strength greater than 105 v/cm at 85°C or higher is required.¹¹⁵ Rothman has calculated the dielectric breakdown for several polyimides and these are also provided in Table 2.6.4.¹²

2.6.6. Mechanical Properties

Glassy or semi-crystalline aromatic polyimides inherently possess high moduli and high strength. Introducing flexible linkages or kinks along the backbone of the polymer reduces many mechanical properties of polyimides. Table 2.6.6 illustrates the high strength nature of some of the polyimides used in the microelectronics area.¹¹⁶

In general, completely aromatic polyimides are preferred for providing both high modulus and higher thermal stability. In addition to the basic mechanical properties, such as modulus and tensile strength, other properties including adhesion, stress and planarizability of the polyimide should be considered. These are explained in more detail below

Table 2.6.6 Mechanical properties of rigid, low CTE polyimides (from ref.¹¹⁶)

	Modulus (kg/mm ²)	Elongation at break(%)	Tensile strength (kg/mm ²)
PMDA / ODA	90	27.4	10.0
PMDA / PPD	430		25
BPDA / ODA	160	13.8	10.8
BPDA / PPD	460	6.3	19.0
BTDA / PPD	440	4.0	12.5
BTDA / ODA	190	8.6	10.6

2.6.6.1. Adhesion

When polyimides are used as an interlayer dielectric for electronic application, one may define four interfaces, a, b, n and d, as shown in Figure 2.6.5.¹¹⁷

The adhesion of a polyimide at each of these interfaces plays an important role in the reliability of the device. The four main adhesive regions to be considered are

(a) Polyimide - substrate adhesion

In order to improve the adhesion of the polyimide to these substrates, several coupling agents, such as amino alkyl trialkoxy silanes or aluminum chelates, have been developed and utilized in the manufacture of electronic devices. These coupling agents are known to substantially increase the adhesion strength between the polyimide and the substrate, as well as to increase both the heat and humidity resistance of the polyimide film as well. Figure 2.6.6. shows the effect on peel strength of the cure temperature of Hitachi PIQ resin.¹¹⁸

Organosilane coupling agents are thought to function by depositing a very thin layer of silane onto the substrate surface by incorporating the primary amino groups into the polyimide structure, forming a chemical bond. One of the main drawbacks of the organosilane coupling agent is that it undergoes thermal degradation in excess of 400°C. In the case of aluminum relating agents, the aluminum compounds convert to a 50 - 200 Å thick Al₂O₃ layer when heated to 350°C in a moist air atmosphere. These provide higher thermal stability than the organosilane agents.¹¹⁹

(b) Polyimide - metal adhesion

Adhesion of polyimides to metal differs greatly according to the kind of metal, as shown in Table 2.6.7.¹²⁰ Adhesion of polyimides to aluminum is superior while the adhesion of polyimides to copper or nickel is not as good, but still in the acceptable range.

(c) Metal - polyimide adhesion

The adhesion strength of metal on PMDA/ODA based polyimides has been observed to be poor, as compared to polyimide on metal. This phenomena is emphasized for polyimides having low coefficient of thermal expansion, seen in Figure 2.6.7. Several effective methods now exist to improve adhesion at the metal / polyimide interface. The importance of clean surface, both in metal and polyimides cannot be over-estimated. The standard approach to improve adhesion for pre-metal deposition is via Ar⁺ back sputtering technique. Plasma treatments can also be used to improve adhesion. Oxygen or tetrafluorocarbon plasma has been observed to increase the adhesion of titanium but not copper, while N₂ plasma has been observed to exhibit remarkable effects on both copper and titanium.¹²¹

(d) Polyimide - polyimide adhesion

Adhesion at the polyimide - polyimide interface is dependant on chemical structure. Multilayering of the polyimide is necessary to increase the thickness of a single dielectric layer. Usually, no special treatment is necessary to promote polyimide - polyimide adhesion. The underlying polyimide is soft cured(B - stage curing) only before the subsequent layer of polyimide is applied. Generally the polyimide - polyimide interface can also be improved by plasma treatment of the underlying polyimide surface.¹²⁰

2.6.6.2. Stress

There are three main factors that contribute to total thin film stress in electronic packaging structures, apart from the normally exhibited intrinsic stresses. These are (a) curing of polymer, (b) solvent evaporation from the wet film, and (c) the thermal expansion mismatch between the polymer and the substrate. Polyimide thin films demonstrate very little stress immediately after the spin coating process. But as the film is

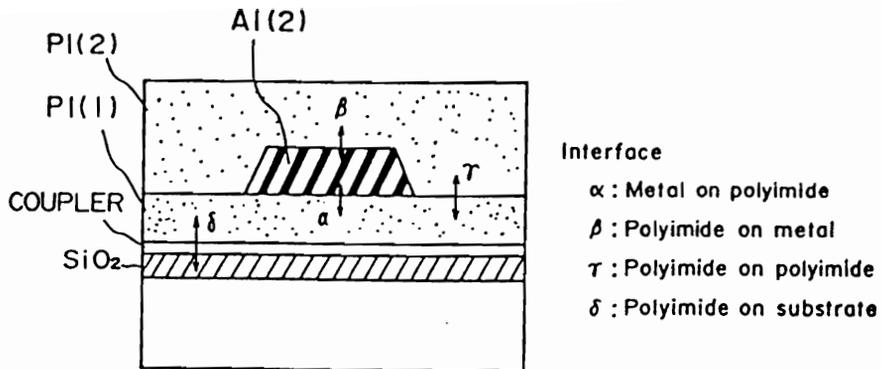


Figure 2.6.5. Cross section of devices and interfaces between polyimide and substrate
(From ref.¹¹⁷)

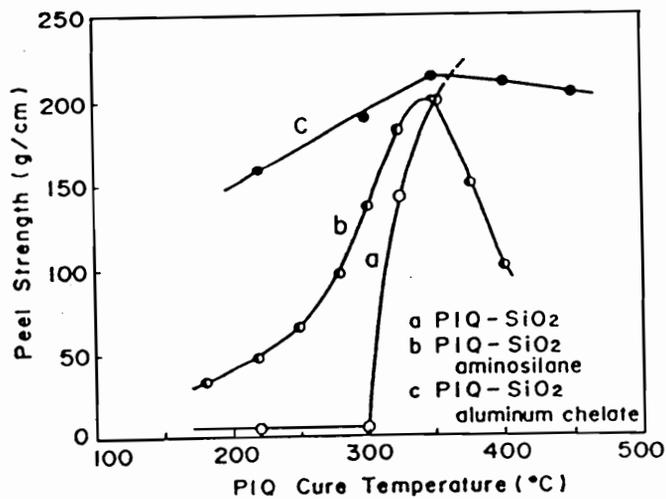


Figure 2.6.6. Adhesion property of PIQ polyimide to SiO₂ (from ref.¹¹⁸)

Table 2.6.7 Peel Strength of PIQ polyimides on metal substrates (from ref.¹²⁰)

Substrate	Adhesive strength (a)
Al	1
SiO ₂	1
Cr	0.8
Ni	0.7 - 0.8
Mo	0.4 - 0.5
Ag	0.2
Au	0.1

a) Adhesive strength normalized by the value of aluminum.

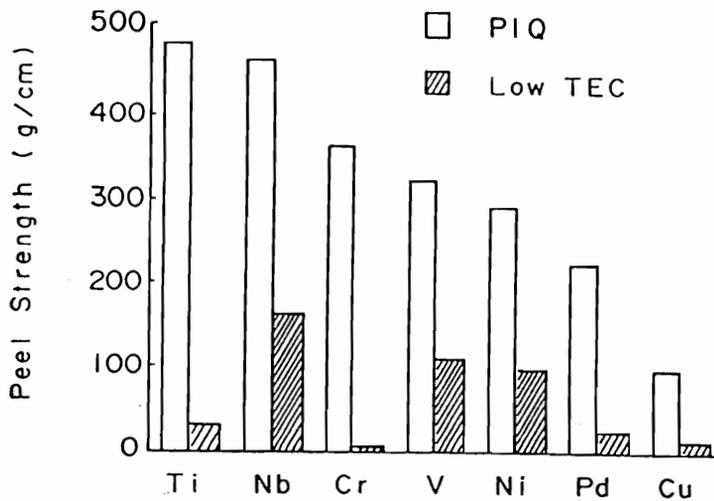


Figure 2.6.7. Peel strength of metal to conventional and low-thermal expansion PIQ polyimide (from ref.¹²¹)

heated, loss of solvent and difference in the coefficient of thermal expansion between polymer and substrate results in strains being incurred in the film during the polymer shrinkage. These strains do not relax, resulting in a large thermally induced stress¹²²

Stresses are elucidated by measuring wafer curvature either with a stylus or optically, using interferometer. Wafer bowing has been used to calculate stresses in polymer thin films.

Stresses can be calculated by

$$s_f = d / (D/2)^2 E_s / 3(1 - P) t_s^2 / t_f$$

where

d = warp measure

E_s = Young's modulus of the substrate

t_s = wafer thickness

t_f = polymer film thickness

D = wafer diameter and

P = Poisson's ratio for substrate

Polyimides with very low residual stress levels are currently preferred for microelectronics applications to prevent delamination of the polyimide film. Hitachi PIQ has been shown to have one of the lowest residual stress levels.⁴⁷

2.6.6.3. Planarization

The single most important property that makes polyimides, attractive as an interlevel insulator, apart from compatibility with existing inorganic dielectric's and ease in processing, is its ability to planarize the underlying topography. This is highly advantageous for use in microscale photolithography when the surface topographies quickly become too severe to be used for multilayer applications. Figure 2.6.8. shows the difference in planarization ability between an inorganic conformal film, such as CVD SiO₂,

with the polyimide dielectric.¹¹⁸ Figure 2.6.8.(a) shows the "steps" formed in the inorganic dielectric material due to underlying topographical features on the substrate, while Fig 2.6.8(b) demonstrates that these steps are eliminated with the use of a polyimide insulator.¹²³ There are obviously many parameters that affect the planarizability of the polyimide. These include:

(a) Polyimide solution properties such as

- (1) Polymer molecular weight
- (2) The solid content of the polyimide precursor solution
- (3) Solution viscosity

(b) Polyimide film deposition process (such as spin coating)

- (1) Dispensed volume of polyimide precursor solution
- (2) Dispensing speed
- (3) Final spin speed

(c) Film shrinkage during processing

(d) Thermal flow during curing

(e) The feature size such as

- (1) Step height
- (2) Pitch

Rothman has defined the degree of planarization (DOP) as

$$\text{DOP} = 1 - t_s / t_A$$

where

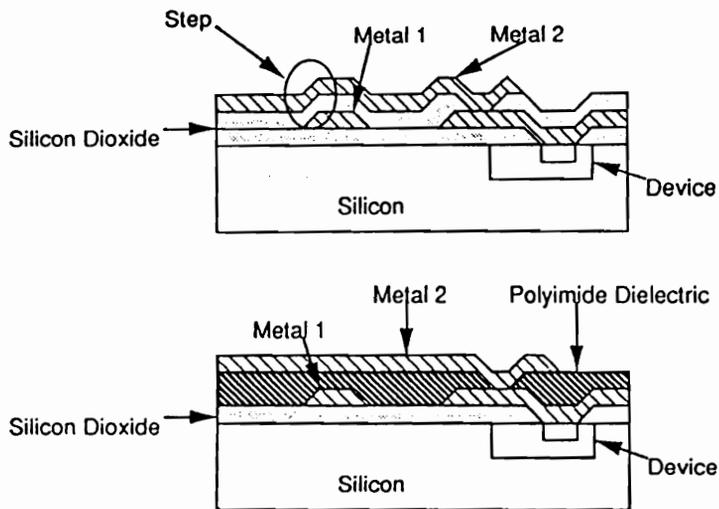


Figure 2.6.8. Polyimide planarization advantage over conventional dielectric's (from ref.¹²³)

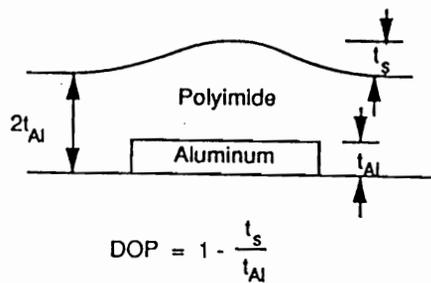


Figure 2.6.9. Degree of planarization definition (from ref.¹²)

t_s = height of the step after planarization and

t_{Al} = is the original aluminum step height

This is shown in Figure 2.6.9.¹²

The degree of planarization has been observed to be directly proportional to polyimide film thickness. By increasing the solid content of the polyimide precursor solution, the degree of planarization increases. Multiple polyimide coating and solution flow properties (as a function of molecular weight, surface tension, polymer entanglement onset) also affect planarization characteristics.¹²⁴ The desired condition for optimum planarization are maximum flow below rigidization, and minimum polymer shrinkage after rigidization. It is believed that loss of perfect planarization in polyimides results from shrinkage once the film no longer flows fast enough to keep up with drying process.¹²³

2.6.7. Chemical Properties

2.6.7.1. Solvent Resistance

Polymers used for insulating films are expected to exhibit resistance to many processing chemicals such as acetone, n-methyl pyrrolidone and various developers. Tessier et al. have looked at the solvent resistance of various dielectric materials and these are provided in Table 2.6.8.¹¹⁰

2.6.7.2. Moisture / Ion Barrier

Organic polymers, such as polyimides, are permeable to moisture and are not hermetic seals. Thus, the moisture uptake of polyimides have been a long-standing reliability issue, due to the possibility of metal corrosion of devices, polyimide surface leakage, polarization and ion motion. Further complications resulting from the impurities present in the polyimide and polyimide chemistry, such as processing, degree of cure and

environmental factors affect moisture uptake. Moisture absorption in several of the polymers that are candidates for polymer dielectric's have been studied by Tessier et.al. and these are provided in Table 2.6.9.¹¹⁰

Studies using UPS and XPS surface spectroscopy have concluded that for polyimides, imidization itself is not sufficient to ensure an intrinsic polyimide system completely devoid of water. Due to the inherent ability of polyimides to absorb water from the atmosphere at room temperature, an annealing step is necessary prior to the additional processing in an attempt to completely remove any water.^{125,126}

2.7. PROCESSING OF POLYIMIDE THIN FILMS

The main advantage of polyimides over other inorganic dielectric's is their relative ease of processing using the existing fabrication line. There are several steps involved in the processing of polyimide thin film. They are (1) application of adhesion promoters on the substrate, (2) application of polyimide precursor solution, (3) curing of polyimide precursor solution to convert it to polyimide film, (4) application of the photo resist, and (5) patterning of the polyimide. Some of these steps are explained in detail in the following section.

2.7.1. Application of precursor solutions

Polyimides are obtained in solution form as a poly(amic acid), poly(amic alkyl ester) or soluble polyimide in NMP. These solutions are deposited on to the substrate by a variety of processes such as spin or spray coating, screening, dipping, or roll coating to produce polyimide films of various thickness (1 to 100 microns). The film thickness requirement for these dielectric layers is a function of dielectric strength, which determines the breakdown voltage of the film. More importantly, the dielectric strength determines the desired capacitance or characteristic impedance of the interconnect. For example, for a

Table 2.6.8. Solubility of several polyimides used in microelectronics (from ref. ¹¹⁰)

Material	IPA	Acetone	NMP	MF - 312 Shipley	Shipley 1400 Resist
DuPont PI2525	+	+	+	+	+
Hitachi PIQ	+	+	+	+	+
Fluorinated PI	+	+	+ / -	+	+ / -
Acetylene Terminated PI					
Fluorinated	+	+	+ / -	+	+ / -
Non Fluorinated	+	+	+	+	+
Silicon - PI	+	+	+	+	+
BCB Resin	+	+	+	+	+
Cibe- Giegy XU-218 Resin	+	+ / -	-		

+ = Soluble, - = Insoluble and + / - = Partially soluble

Table 2.6.9. Moisture Absorption Using Weight Gain Measurements (from ref. ¹¹⁰)

Material	Percent Gain (%)
DuPont PI 2525	
Hitachi PIQ resin	1.1
Acetylene Terminated PI	1.4
Silicon PI	0.9
Fluorinated PI (XUP3119)	0.7
Low Stress PI (DuPont PI2611D)	0.5
BCB resin	0.3

material having a dielectric constant of 3.5 and dielectric strength of 10^6 volts/cm, a thickness layer of approximately 1 to 2 microns is required for multilayer devices such as VLSI and memory IC chip. For obtaining polymer thicknesses in the sub micron to the 10 micron range, spin coating has been the most common technique.

As mentioned, spin coating widely used for depositing uniform films of photoresist in IC processing. Various factors that affect the polymer film thickness and uniformity in the spin coating process have been modeled.¹²⁷ These are (a) viscosity of the polymer solution, (b) volume of the solution dispersed on the substrate, (c) angular speed of spinning, and (d) the spin time. The spinning speed has been the most sensitive variable for controlling film thickness. The largest practical film thickness achievable by spin coating is on the order of 15 microns. Thicker films such as those required for interlayer dielectric's, are achieved by multiple spin coatings with a cure temperature of at least 150°C between coats, although it is very difficult to spin coat uniformly thick films using this process. It is also limited to square or round substrates of only a few inches in diameter and with no large surface topography.

Spray coating has been used to overcome the limitation of spin coating process so that thicker uniform films can be deposited . Very few detailed process descriptions of spray coatings are available in the literature.¹²⁸ Honeywell has developed a spray coating process by which they had deposited 1 to 15 micron thick polyimides with an accuracy of +/- 1 micron (m) with 60% planarization achieved after three coats.

Polyimides can be accurately spray coated by passing a spray nozzle over the substrate which moved on a conveyor belt at right angles to the nozzle motion. Here also, the uniformity and thickness of the film depends on various parameters such as solution viscosity, concentration, flow rate, diameter, and shape of the spray nozzle, its distance from the substrate, atomization pressure, conveyor speed, and number of passes of the

spray nozzle over the substrate.

Other alternative processes such as screen printing and vapor deposition, are also available and offer the possibility of producing uniform, defect free, conformal films that can be cured in situ during deposition.¹²⁹⁻¹³¹

2.7.2. Curing of precursor solutions

Once the poly(amic acid) solution is applied on the substrate it generally goes through a heating or baking cycle in order to convert the poly(amic acid) solution to polyimide, with simultaneous removal of the solvent NMP.

The first stage of the heating cycle is typically performed at 90 to 120°C for 30 mins. to 1 hour in a convection or forced air oven. Even though the boiling point of NMP is 205°C, its vapor pressure allows the bulk of the solvent to be removed during its low temperature heating cycle. This is followed by a second baking step at around 200°C for 1 to 2 hours, also in a convection air oven. This step initiates the imidization reaction of the poly(amic acid) with the evolution of water as the byproduct. During this step most of the water and NMP are removed. The curing of the polyimide is usually completed at around 350 to 400°C, usually under a nitrogen atmosphere for about 15 to 30 minutes, depending on the chemical composition of the polyimide. The final heating step is to complete the imidization reaction for complete removal of solvent and water from the polyimide film. It has been shown that two polyimide moieties (four imide bonds) within the polyimide chain can hydrogen bond as many as seven water molecules which, even though not chemically bonded, are difficult to remove especially in a rigid, fully imidized chain network.^{132,133} Because of this reason, some manufacturers prefer a quick super hot process, i.e., a 420 to 450°C bake for a few minutes.

2.7.3. Patterning

Polyimide thin films must be patterned to open via holes for metal contacts, through techniques such as a wet or dry etching process through a photo-lithographically defined mask, direct photo patterning of photosensitive polyimides, or layer ablation. The wet and dry etching is most widely and the process steps involved in this method is shown in Figure 2.7.1.¹³⁴

2.7.3.1 Wet etching process

One of the earliest techniques used for polyimide processing was the wet etching process. The initial pattern is first defined by developing a positive or negative photoresist film on the polyimide. The unmasked polyimide is then selectively dissolved and the photoresist is stripped. Fully cured polyimide films are etched with a solution of hydrazine hydrate ($\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$).^{47,135} Additional compounds, such as ethylene diamine have been added to increase the etch rate with time. The partially imidized state used alkaline solutions such as tetraalkyl ammonium hydroxide, sodium hydroxide or potassium hydroxide. The residues left by the alkaline solutions are usually neutralized with acetic acid and water rinses.¹³⁶

The primary limitation of the wet etching process is the low resolution and small aspect ratio (thickness / width) of the patterned features. Another drawback of wet etching is that, with the exception of hydrazine, all the other etchants require partially cured polyimide films. Since the etch rate depends on the degree of cure, it is difficult to accurately reproduce etch rates and control the pattern geometrics. Finally, additional curing of the partially imidized film at elevated temperatures could further shrink the film, resulting in additional loss of resolution.

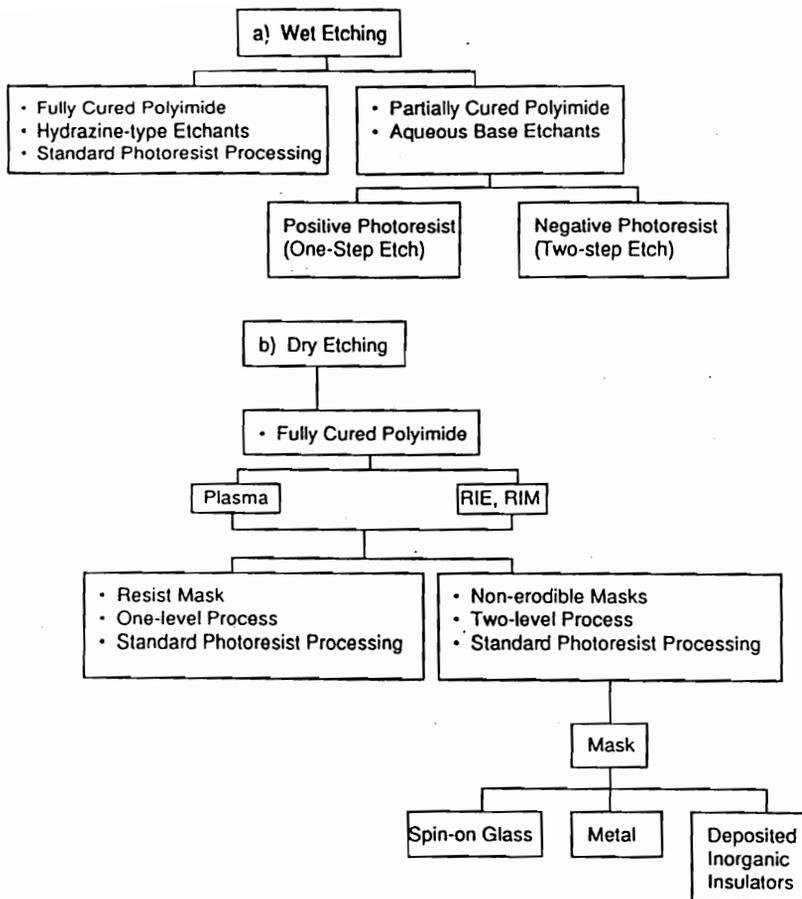


Figure 2.7.1 Polyimide Etching Techniques (from ref.¹³⁴)

2.7.3.2. Dry etching process

The dry etching process overcomes the limitations associated with wet etching. Hence, the polyimide may be etched using “dry” vacuum processes such as plasma etching or reactive ion etching (RIE), in which the substrates are placed on the lower electrode in a parallel plate system sustaining an RF plasma.^{112,137,138} Other processes include reactive ion beam etching (RIBE), in which a beam of reactive ions (e.g., O⁺) or inert ions (Ar⁺) are accelerated toward the substrates, which may be flooded with a reactive gas such as O₂.¹³⁹ In all these processes, the etching reaction is initiated by ions that are accelerated perpendicular to the film surface, thus producing high aspect ratio features with nearly vertical side walls in fully cured polyimide films. These processes are more reproducible than wet etching and can be varied to accurately control characteristics such as the etch rate, the selectivity for etching different material and the side wall angle of etched features.

The most promising future technique identified thus far for patterning a polyimide film is direct patterning by laser ablation.¹⁴⁰

2.8. APPLICATIONS FOR POLYIMIDE THIN FILMS

Polyimide thin films are mainly used in four areas of application (a) as intermetal dielectric's for integrated circuits, (b) in electronic packaging, (c) as passivation and protective layer and, (d) as a fabrication aid. These are explained in detail in the following sections

2.8.1. Intermetal dielectric's for integrated circuits

One of the most important applications for polyimides in electronics is as intermetal dielectric's in multilevel interconnections on integrated circuits. Chemical vapor deposited silicon dioxides (CVD oxides) have been the most widely used intermetal dielectric's. In recent years, however, polyimides have been successfully used in this application.

The chemical, physical, mechanical and electrical properties of polyimides were discussed in earlier sections. Many of the mechanical and electrical properties of SiO₂ and polyimides are comparable, and these are provided in Table 2.8.1.¹⁴¹ As can be observed from the Table, the coefficient of thermal expansion of the polyimide is approximately an order of magnitude higher than the SiO₂. The thermal stability and Young's modulus of SiO₂ are higher than those of polyimides. The tensile strength and electrical properties (volume resistivity, dielectric strength and dielectric constant) of SiO₂ and polyimides are similar. In fact, the dielectric constant of polyimides are even lower.

Polyimides possess several advantages over the CVD oxides (1) polyimide thin films ranging from 0.5 to 5 microns can be deposited on the silicon wafer by spin coating followed by curing, (2) the capability of polyimide films to planarize the topography of the substrate, the most important advantage over CVD oxides is better because planarization facilitates the patterning of contact vias that is critical to the success of multilevel metallization, (3) since thicker polyimide films can be formed without cracking (i.e. residual stress is less than fracture strength), the pinhole density of the film is small,¹⁴² and (4) since thick polyimide films are used, the interlevel capacitance is reduced, which enhances high speed operations of integrated circuits. By using 1.7 micron films of PI-2545 films, the interlevel capacitance has been reduced to $2.66 \times 10^{-9} \text{ F / cm}^{-2}$, which is half that of the conventional oxides.¹⁴³

The main issues related to the use of polyimides as intermetal dielectric's are water absorption and polarization. It has previously been discussed that water absorption has a significant effect on the electrical properties of polyimides. To minimize water absorption, polyimide thin films must be adequately dehydrated and finally imidized. To prevent water absorption after cure, thin passivation films of silicon nitride or silicon oxide are deposited on the polyimides as moisture barriers. Of the two, silicon nitrides appear to be more effective for this purpose.¹⁴⁴

Table 2.8.1 Physical properties of polyimides and silicon dioxides(from ref. ¹⁴¹)

Properties	Polyimides	SiO ₂
Coefficient of thermal expansion (1 /°C)	$5 * 10^{-5}$	$4 * 10^{-7}$
Thermal stability (°C)	475 - 500	1700
Young's modulus (GPa)	3	70
Tensile strength (GPa)	0.1 - 0.2	0.2
Volume resistivity	10^{16}	$> 10^{16}$
Dielectric strength (v / cm)	10^{16}	$10^6 - 10^7$
Dielectric constant	3.5	3.7

Polyimides are long chain organic polymers that contain polarizable components such as carbonyl groups. Under the influence of an electric field, the dipoles in the polymers could preferentially be aligned, thus inducing an opposite charge at the interface. The charge effects can cause inversion of underlying silicon and, consequently, undesirable communication between doped areas.^{145,146} Effects of polyimide polarization on a typical bipolar structure are shown in Figure 2.8.1., which shows a parasitic channel formation due to polyimide polarization. The degree of polarizability in polyimides appears to be related to chemical structure, with the least hygroscopic polyimide being the least polarizable.¹⁴⁷ Polarization has been a major reliability concern for polyimide applications. The problem, however, has been addressed by eliminating structure within a common silicon island, limiting the use of polyimides to low voltage applications, or by adding a silicon dioxide film as an underlayer of the polyimide that increases the parasitic device threshold.¹⁴⁸

2.8.2. Electronic packaging

Polyimides are used in a variety of applications related to the packaging and interconnections of integrated circuits. Polyimide / glass composites for printed circuit boards are one of the most important alternatives to the standard epoxy / glass boards.¹⁴⁹ The main advantage of polyimide / glass is its high thermal stability, which permits the use of high temperature soldering processes in assembly operations. Polyimide adhesives, sometimes filled with thermally or electrically conductive particles such as silver or ceramic, are also becoming a widely used alternative to epoxies for die attachments, because of their good thermal and chemical stability and higher degree of purity (less chlorine content).¹⁵⁰ Free standing polyimide films (e.g. Kapton) are used as flexible substrates for multichip circuits¹⁵¹ and for type automated bonding (TAB) lead frames. TAB is becoming a widely used alternative to wire bonding because it can achieve a higher

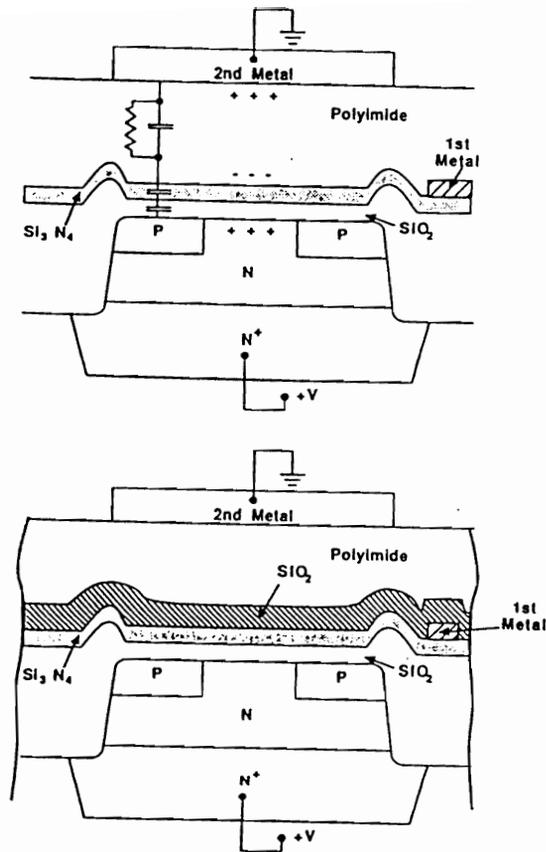


Figure 2.8.1. a) Effects of polyimide polarization on typical bipolar structure, b) one possible solution to the polarization problem (from ref.¹⁴⁵)

a) High performance packaging requirements

The high circuit densities and switching speeds of advanced very large scale integration (VLSI) and GaAS IC's have created a need for new technologies to package and interconnect these devices. For very high performance systems, multichip packaging approaches are being used to achieve greater chip density, reduce the number of external interconnections and the interconnect length, and thereby reduce the delay time and power consumption required to drive the signals between chips. The high interconnect density of multichip packaging requires processes that can define high resolution conductor patterns in multichip layers on relatively large substrates. A high density interconnect technology that is being actively developed throughout the electronics, computer and IC packaging industries is based on the use of thin film IC - like processes to pattern multichip layers of a thin film conductor such as gold, or copper and a polymer dielectric, which are primarily polyimides.¹⁵²⁻¹⁵⁶

The thin film multilayer (TFML) interconnect structures can be fabricated on a variety of substrates and incorporated into a variety of packaging designs. The packaging structure shown in Figure 2.8.2. has been proposed by Honeywell^{106,154} and is representative of many of the packaging approaches being implemented in the industry. In the first approach, the TFML interconnections are patterned on a multilayer confined ceramic substrate. This may contain additional structures, such as internal metal layers for power and ground distribution, a grid array of pins for connecting the package to a printed wiring board (PWB), metallized strips to provide thermal contact to the PWB, and a metallized ring around the perimeter for attaching of a seal ring and lid for hermetic sealing. In the second approach, the TFML interconnections are patterned on a blank metal or ceramic substrate, which is then mounted into a hermetically sealable package such as a metal flatpack with perimeter leads. In the third approach, TFML structures are fabricated on large substrates to create high-density board level interconnections between single or

multichip packages. These approaches are also shown in Figure 2.8.2.

In all of these packaging approaches, the high-density interconnections are patterned in TFML structures of copper (or other high-conductivity) conductor and polyimide dielectric.

b) Advantages and applications of TFML interconnections

TFML interconnections offer a number of inherent advantages over other interconnect technologies. Table 2.8.2.¹⁵⁷ compares the material properties, geometry's, and electrical properties of TFML interconnects with the two primary competing technologies cofired ceramic and multilayer thick film. First thin-film patterning processes, such as photolithography and dry etching, can define higher resolution and higher aspect ratio features in the conductor and dielectric materials than the screen printing and hole-punching processes used for cofired ceramic or thick film. The TFML geometry's result in high interconnect densities and low interconnect resistance and capacitance. Second thin-film metal deposition processes, such as sputtering, permit the use of high conductivity metals (Cu, Al) and can achieve nearly bulk resistivity in thin films, as compared to the lower conductivity W and Mo pastes used in cofired ceramic technology or the Cu and Au pastes used for thick films. Third, from a manufacturing standpoint, TFML technology offers cost advantages over thick film and cofired ceramic technology by replacing labor-intensive screen printing processes with automated semiconductor processes, and by replacing hard-tooled punches or screens with fast-turnaround photolithographic masks.

The TFML technology is also highly flexible in that it can be applied to a wide range of substrates, interconnect geometry's, and performance requirements. It is being widely developed for multichip packaging of VLSI, VHSIC, and GaAs integrated circuits,^{21,106,112} and for high-density hybrid circuits employing lower performance integrated circuits.^{129,155} The TFML technology also offers a number of advantages for

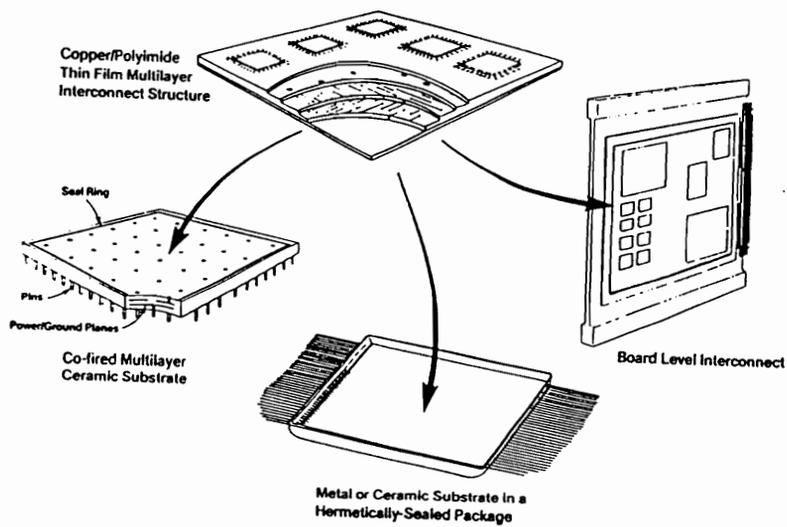


Figure 2.8.2. Different IC packaging schemes incorporating copper / polyimide thin film multilayer interconnections (from ref.¹⁵⁴)

Table 2.8.2. Comparison of multichip packaging technologies(from ref.¹⁵⁷)

	Cofired ceramic ^b	Thick-film multilayer ^b	Thin-film multilayer ^b
Conductor material ^a	W (Mo)	Cu (Au)	Cu (Au, Al)
a) Sheet resistance	0.01	0.003	0.0035
b) Thickness (μm)	15	15	5
c) Line width (μm)	100	100-150	25 ± 10
d) Pitch (w / vias) (μm)	750 ± 250	250	125 ± 50
e) Max no. of layers	7 ± 30 +	5 ± 10	5 ± ?
Dielectric material	Al ₂ O ₃	Glass / ceramic	Polyimide
a) Dielectric constant	9.5	6.5-9	3.5
b) Thickness / layer (μm)	250-500	35-65	10-25
c) Via diameter (μm)	200 ± 100	200	25
Propagation delay (ps / cm)	102	90	62

^a Alternative conductor materials are in parentheses; properties are given for primary conductor materials.

^b Geometry's are given for current standard technology; an arrow (±) indicates demonstrated advanced technology.

board-level interconnections between surface-mounted single chip packages or bare chips. Furthermore, the TFML materials system and process technology can be extended to even finer geometry's required for wafer scale integration,¹⁵⁶ or for high-density optical interconnections using thin-film waveguides.^{158,159}

2.8.3. Passivation and Protection

Polyimides have been increasingly used as passivation materials for protecting IC's and device circuits. Traditionally, SiO₂ and Si₃N₄ have been the most widely used passivation materials. These inorganic materials, however, require higher processing temperatures and often cannot provide adequate step coverage. The advantages of using polyimides as passivation materials are spin cotability, patternability, lower processing temperature, good chemical resistance and thermal stability, and planarizability (i.e., providing good step coverage).

The passivation layers must provide protection from physical and mechanical damage, act as a barrier to water molecules and ionic contaminants, and must not affect the performance of ICs and device circuits that it protects. It has been noted that a thin-film overcoat can induce significant mechanical stress, which affects the functional characteristics of the device circuits, e.g., the threshold voltage of a metal oxide silicon transistor.¹⁶⁰

Polyimides have been used as particle barriers to prevent soft errors of memory devices resulting from a particles emitted by a trace amount of naturally occurring thorium and uranium isotopes in packaging materials.^{161,162} A layer of polyimide overcoat with a thickness $\geq 75 \mu\text{m}$ stops most a particles emitted from the packaging materials.

Polyimides have been used to passivate thin-film microwave hybrid circuits.¹⁶³ It is known that electromigration has been one of the principal failures modes in ICs. Electromigration is a mass transport occurring in metal thin-film conductors due to the

momentum exchange between conduction electrons and the metal atoms as an electric current is passed through the conductor.¹⁶⁴ Electromigration is typically characterized by resistance changes and open circuit failures, and is often attributed to void formation in the conductor. It has been found that a passivation layer on top of the metallization can enhance the reliability of the semi-conductor.¹⁶⁵ Although CVD SiO₂ has been the most commonly used passivant for ICs, recent studies indicate that polyimide passivation can significantly retard electromigration, and thus enhance the reliability of the underlying conductors.

2.8.4. Other applications for polyimides in microelectronics

Because of their excellent thermal properties, chemical stability and good processibility, polyimides have found a number of other applications in microelectronics. An important application of polyimides is their use as a temporary masking or planarizing layer to aid in the fabrication of microelectronics structures. Polyimides are an ideal planarizing material because a) they can be deposited over a wide range of thicknesses, b) they have good planarizing properties c) they and do not degrade at high temperatures or in the presence of the chemicals involved in subsequent processing steps.

Polyimides can also serve as masks for dry etching processes, in which relatively thick masking layers are required, or they can serve as a mask for ion implantation^{166,167} or ion-beam lithography.¹⁶⁸ Polyimides have been used as a flexible substrate for X-ray masks.¹⁶⁹ The good dimensional stability of polyimides and their transparency to X-rays makes them well suited for this application.

2.9. FUTURE TRENDS FOR POLYIMIDE USE IN MICROELECTRONICS INDUSTRY

The future of polyimides in microelectronics will be driven mainly by cost factors

and the availability of high performance materials. Improved performance translates to smaller, faster and more reliable electronic products. In order to meet these needs, very important developments are occurring such as very large scale integration (VLSI) and more specialized customization using application specific ICs (ASICs).

A major recent trend in the electronics industry has been to reduce the dimensions of the devices, (usually transistors), and thus reduce the size of the ICs. Reducing a device's linear dimensions by a factor of four, doubles operating speed, reduces power consumption by a fourth and the cost / performance ratio improves by a factor of approximately eight. However, this requires the substrate circuitry to be much finer than is presently available.

Satisfactory operation at high signal speed depends to some extent on track geometry, but largely on the substrate material. Digital processors which operate by means of a stream of pulses, are now functioning at higher speeds (10-100 MHz clock rates). At these rates, signals are propagated as an electrical wave system traveling through the substrate, the air and the metal conductor. Thus, the substrate now becomes a key factor.

The dielectric constant of the substrate is the prime variable because the propagation speed of the signal is inversely related to the square root of the dielectric constant. Figure 2.9.1 shows the effect of dielectric constant for various materials as a function of signal propagation speeds.¹⁷⁰ At these speeds, the system has to be designed as a transmission line that must match the impedance of the devices used. Impedance mismatch can lead to reflected signals, and hence to signal distortion. The characteristic line impedance is also dependant on the dielectric constant, and for these devices, higher impedance's are required and, therefore, low dielectric constant substrates are needed.

To increase impedance for device matching, narrow and much finer circuit lines or tracks are desirable. This not only increases, the impedance but also increases the density of leads from higher functional devices. This increase in density helps to decrease the

overall size of the IC package. However, as tracks get closer, the problem of crosstalk worsens. Crosstalk, as discussed earlier, has also been found to be directly proportional to the dielectric constant of the substrate.

The design of these high speed interconnections involves calculating the separation between tracks and ground planes, as well as controlling dielectric thickness. It is therefore vital that the material be consistent, so that these dimensions remain stable and uniform and tolerances can be maintained, providing more reliable electronic products.

As discussed in previous sections, polyimides play a very important role as an interlevel dielectric layer. The performance advantages offered by polyimides include (1) high-density patterning, due to the planarization of polyimides; and (2) high reliability, due to the excellent thermal, chemical and mechanical stability. When compared to ceramics, polyimides also have a lower dielectric constant, which is very important in increasing the speed, density and reliability requirements of ICs. It would be of great interest to reduce the dielectric constant of the polyimide further to about two and still maintain the excellent properties of polyimides for high speed signal propagation.

The dielectric constants of commercially available polyimides presently used as state-of-the-art materials for interlevel dielectric's generally range from 3.2 to 4.0, depending upon measurement frequency and moisture content.¹⁷¹ It has been shown in the literature that dielectric constants of less than 3.2 can be obtained by reducing the interactions between the linear polyimide chains and by incorporating fluorine into the polymer backbone.¹¹¹ One of the first commercially available fluorinated polyimides for electronic applications was produced by DuPont and was based on 2,2'- bis (3,4-dicarboxyphenyl) hexafluoropropane dianhydride / oxydianiline (6FDA / ODA) backbone chemistry.¹⁷² Early work by DuPont in the area of fluorinated dianhydrides and diamine monomers led to the development of a polyimide based on 2,2- bis (3,4- dicarboxyphenyl) hexafluoropropane dianhydride / 2,2- bis (4- aminophenyl) hexafluoropropane (6FDA /

6FDA) shown in Figure 2.9.2.¹⁷³ Although these materials possessed good thermal stability, a low dielectric constant of 2.7, low moisture uptake (< 1.0 %) and formed colorless creasable films, their processing utility has been somewhat limited by poor mechanical properties and extreme solvent sensitivity.

In an effort to improve solvent resistance, 6FDA / 6FDAM polyimides were modified by incorporating aryl ether segments. The resulting 2,2- bis (3,4-dicarboxyphenyl) hexafluoropropane dianhydride / 2,2-bis [4-(4-aminophenoxy)phenyl] hexafluoropropane (6FDA / BDAF) polyimide had a dielectric constant of 2.8 and a level of moisture uptake of <1.0 %. Cured coatings of the 6FDA / BDAF polyimide displayed less solvent sensitivity towards NMP, ketones, THF and diglyme than 6FDA / 6FDAM based polyimides. However, a significant reduction in T_g (260°C) was observed, due to increased chain flexibility afforded by the aryl ether segments.¹⁷⁴

In order to improve the glass transition temperature of 6FDA / BDAF materials, copolyimides containing various amounts of para phenylene diamine (PPD) have been synthesized. As expected, these materials demonstrated higher glass transition temperatures than the 6FDA / BDAF materials, but possesses higher dielectric constants and greater moisture absorption than the corresponding base 6FDA / BDAF polyimides.⁷⁶ More recently, rigid polyimides with improved solvent resistance and lower moisture absorption have been synthesized from new diamines based on 2,2'- bis (trifluoromethyl)-4,4'-diaminobiphenyl (TFMB)^{175 176} (Figure 2.9.3. a) and 2,2'-bis (fluoro alkoxy) benzidines (Figure 2.9.3. b).¹⁷⁷

These diamines have been polymerized with dianhydrides such as 6FDA, PMDA, BPDA, and also with some new stiff dianhydrides such as 9,9- bis (trifluoromethyl) xanthene-2,3,6,7-tetracarboxylic dianhydride (6FCDA) (Figure 2.9.4. a) and 9-phenyl-9-(trifluoromethyl) xanthene-2,3,6,7-tetracarboxylic dianhydrides (3FCDA) (Figure 2.9.4.

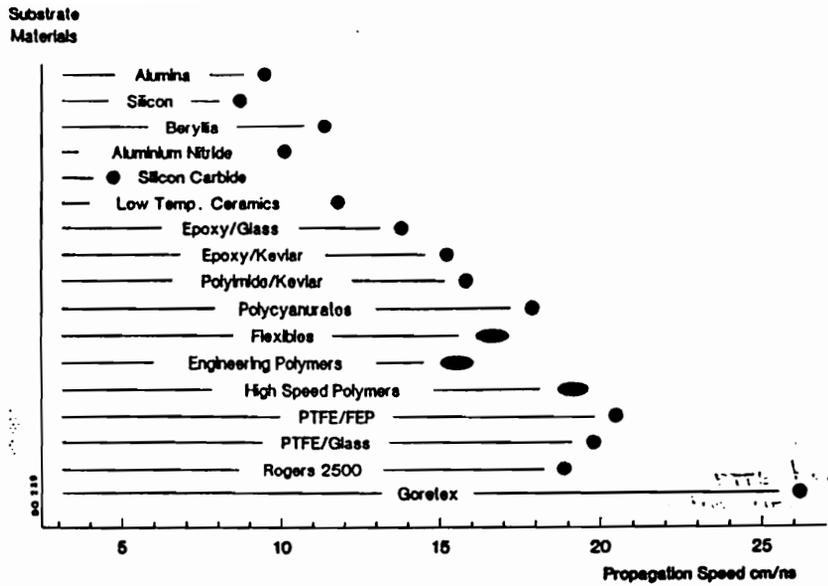


Figure 2.9.1. Propagation Speed of substrate Materials (from ref.¹⁷⁰)

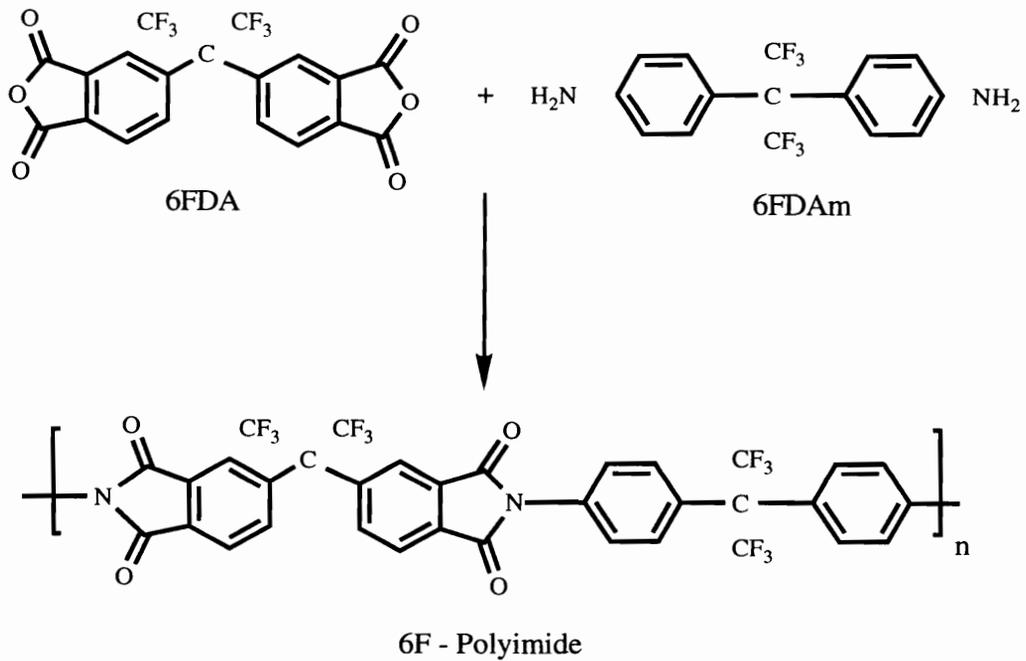
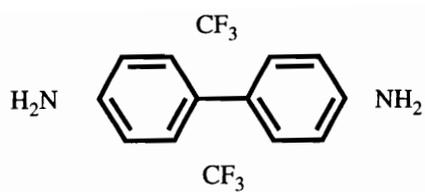


Figure 2.9.2. Chemical structure of 6FDA / 6FDAm based polyimide(from ref.¹⁷³)

b).¹⁷⁸ Polyimides obtained from TFMP were observed to have very good thermal stability > 475°C in air, a low dielectric constant of about 2.5, low water absorption and good solvent resistance, as shown in Table 2.9.1.¹⁷⁹ But polyimides prepared from 2,2'-bis(fluoro alkoxy)benzidines to have lower thermal stability than the polyimides obtained from TFMB. In general, polyimides obtained from fluorinated dianhydrides and diamines have a glass transition temperature ranging from 230 to 375°C with more rigid diamines affording higher Tg's. While these materials generally possess good thermal stability, low dielectric constants (\approx 2.5 to 2.9) and low water absorption (< 1 to 2%), there are nevertheless several drawbacks to using fluorinated polyimides. These advantages include low mechanical properties, very high sensitivity to solvents,(especially the fluorinated aromatic polyimides) and, in general, higher coefficient of thermal expansion compared to the non-fluorinated polyimides. Fluorinated monomers are also generally very difficult to synthesize and hence they can be very expensive. The lowest dielectric constant that has been reported to date for fluorinated polyimides is about 2.4.

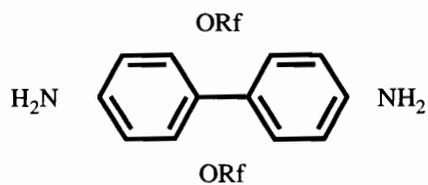
In order to further decrease the dielectric constant to about 2, and to obtain a better property balance of the polyimide, polyimide-Teflon composite blends have been prepared.¹⁸⁰ Initial work by Goff et. al. involved the use of Teflon FEP and polyimides based on pyromellitic dianhydride / oxydianiline (PMDA / ODA) and 6FDA / ODA backbone chemistries. Dispersion of Teflon FEP powder and poly(amic acid) were prepared in NMP. The dispersion, when cured, resulted in opaque films. The incorporation of Teflon FEP afforded reduced dielectric constants with lower levels of moisture absorption, compared to the pure polyimide as shown in Table 2.9.2. However as the level of Teflon FEP was increased, the dielectric constant dropped, and the mechanical properties were observed to decrease markedly.

Recently W.L. Gore and associates have commercialized a very interesting product



TFMB

a

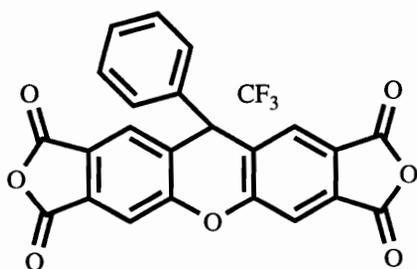


Rf = CF₃, CF₃CF₂H &

CF₂CFHOCF₂CF₂CF₃

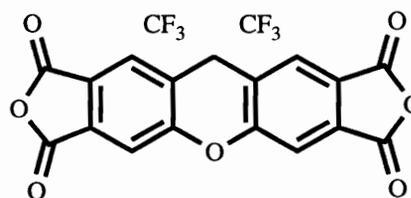
b

Figure 2.9.3. Structure of new rigid diamines (from ref.^{175,179})



3FCDA

a



6FCDA

b

Figure 2.9.4. Structure of new rigid dianhydrides (from ref.¹⁷⁸)

Table 2.9.1. Characteristics of polyimides derived from new rigid monomers (from ref.

179)

	% fluorine	CTE ppm /°C	% H ₂ O abs @ 85% RH	Dielectric constant @ 1MHz	TGA 5% wt. loss in air (°C)
6FDA / 6FDAM	30.7	48	1.1	2.4	524
PMDA / TFMB	22.7	-3	1.9	2.6	592
BPDA / TFMB	19.7	20	1.3	2.9	580
6FDA / TFMB	30.7	6	1.2	2.5	473
6FCDA / TFMB	30.7	6	1.2	2.5	473
3FCDA / TFMB	22.8	13	1.8	2.7	484

based on Teflon called Goretex[®], a fiber containing air pockets that reduce the dielectric constant of Teflon considerably from 2.1 to 1.3.¹⁸¹ When air, which has a dielectric constant of 1, is introduced into the Teflon matrix, as in the 'Goretex' fiber, the signal propagation speed was observed to increase greatly to 26 cm / nanosecond, which is 88% of the speed of light due to the lower dielectric constant of the fiber.¹⁷⁰ This indicates that when air is introduced into any polymer, the dielectric constant of the polymer can be decreased, corresponding to the amount of air in the matrix. Thus, foamed polymers are expected to have lower dielectric constants than unfoamed polymers. Therefore one way of reducing the dielectric constant of polyimides without incorporating fluorine would be through the generation of polyimide foams.

2.10. POLYIMIDE FOAMS

Polyimide foams have existed since 1966, when Hendrix from DuPont produced a foamed polyimide by beating air into a gelling polyimide precursor.¹⁸² This resulted in a spurt of research in the field of polyimide foams targeted mainly towards the aerospace and transportation industries. The excellent flame resistance of these polyimide foams was expected to lead to extensive use as heat shields, thermal acoustical insulation materials, floor panels, materials for radome construction and resilient foam seat cushion materials. Foams targeted toward the aerospace and transportation industries were generally prepared by (a) the use of a blowing agent, (b) the inclusion of microspheres i.e. syntactic foams, (c) the partial degradation of a polyamic alkyl ester and, (d) the formation of the polyimide from the diisocyanate - dianhydride route.

2.10.1. Utilization of chemical blowing agents

Foamed polyimide particles have been produced by incorporating a blowing agent

Table 2.9.2. Characteristics of Polyimide - Teflon composites (from ref.¹⁸⁰)

Comp.	Teflon		Dielectric constant	% H ₂ O absorbed	Tensile st. (PSI)	Elong. (%)	E (KPSI)
	wt. %	vol. %					
Teflon FEP	100	100	2.15	< 0.5	3000	300	70
PMDA / ODA	0	0	3.37	2.2	12000	25	202
PMDA / ODA- Teflon FEP	35	26	-	-	8200	20	178
	48	37	3.12	1.4	7700	21	150
	60	49	3.01	1.1	-	-	-
	73	63	2.85	1.0	5500	11	140
6FDA / ODA	0	0	3.06	1.5	10900	15	270
6FDA / ODA- Teflon FEP	38	28	-	-	7300	9	192
	58	47	2.58	-	4100	5	150
	68	54	2.5	-	3800	5	140

into a solution of a polyimide - forming prepolymer, such as the poly(amic acid), and curing the resulting mixture.^{182,183} The blowing agents used were gas producing acids such as oxalic, malonic, citric or formic acid. During the curing step, the acid decomposes to give bubbles of carbon dioxide and/or carbon monoxide in the solution; and, as the solution foams, it is converted to the solid, porous polyimide when exposed to curing temperatures. Though foams were obtained using this process, high temperatures were required (about 350°C) for complete degradation of the blowing agents and this resulted in foams having a rather coarse cell structure consisting of voids and fissures. The use of the gas-liberating acids for production of foams was also difficult to control, resulting in foamed polyimides having both open and closed cells.

2.10.2. Polyimide foams by the inclusion of microspheres

Syntactic foamed plastics or spheroplastics are a special kind of gas filled polymeric material. This material is classified as a foamed plastic because it is similar in structure to cellular gas-expanded plastics in that it is heterophase, gas solid system. These materials can also be thought of as reinforced or filled plastics and are thus referred to as physical foams.¹⁸⁴

A syntactic foam consist of hollow microspheres (micro balloons) embedded in a polymer matrix called the binder. Several polymers such as epoxy, phenolic's, polyesters, silicones, polyurethanes, polyimides, polyamids, polyphenalene sulfides, have been used as binders to date. Low molecular weight crosslinkable polyimide oligomers have also been made with various materials such as glass - carbon, metals, ceramics, polymers and from phenolic's resins.

The size, quantity and distributive uniformity of the fillers determine the cellular structure of the syntactic foams. Because the micro balloons are completely closed empty spheres, the resulting material is also expected to possess completely enclosed cells. Hence, in comparison to reticulate or co-open cell foamed plastics, these materials are

called "absolute" closed cell foams. The absence of micro structural anisotropy based on size and shape of the micro balloons also provides the valuable properties for the syntactic plastics. These materials demonstrate better strength to weight ratios than conventional "chemically" foamed plastics, they exhibit very low water absorption, and they can withstand a considerable amount of hydrostatic pressure. These materials are lighter and have been observed to have lower residual stress in the foamed state.

By changing the filler type, the binder, the binder-filler ratio and the manufacturing techniques, the syntactic materials with widely varied properties can be obtained. Syntactic foams with apparent densities ranging from 0.5 to 1 g/cm³ have been made. An excellent review on syntactic foams is also available in the literature.¹⁸⁵

Recently Koenig et. al. have reported the development of polyimide based three-phase syntactic foams.¹⁸⁶ These composites consists of hollow microspheres bonded together with a limited amount of polymer, which does not form a continuous matrix. The void space is a third phase that is intentionally introduced into the polymer matrix. The lowest practical density possible with two-phase syntactic foams containing glass microspheres is limited to the range of 0.5 to 0.6 g/cm³. Densities below this value can be achieved by the three-phase systems. Kenig et. al. have developed high temperature stable syntactic foams and have measured both their mechanical and electrical properties especially the dielectric constant. Using the above technique, polyimide with dielectric constant of 1.3 has been synthesized.¹⁸⁷

2.10.3. Foams by the partial degradation of poly(amic alkyl ester)

Apart from poly(amic acids), poly(amic alkyl ester) can also be considered as polyimide precursors. Poly(amic alkyl ester), as described earlier are prepared by reacting the diacylchloride diester of the corresponding dianhydride with the respective diamines in the presence of a tertiary amine, such as a acid receptor. Heating the poly(amic alkyl ester)

results in cyclization of the precursor to the polyimide, with simultaneous loss of the corresponding alcohol from the ester moiety. The resulting alcohol generated has been used as the blowing agent to generate polyimide foams.^{188,189}

The process initially involves, the synthesis of the monomeric precursors by first reacting the dianhydride with an ester fusing agent to form an alkyl diester. The preferred esters are methyl, ethyl, propyl and isopropyl and/or other alkyl alcohol's. Ethanol is in many cases preferred because of its widespread availability, low cost, low toxicity and other desirable attributes. The esterification reaction is followed by the addition of the aromatic diamines, which are allowed to dissolve in the reaction mixture. The temperature is kept below the reflux temperature of the esterifying agent, which is low enough to avoid polymerization. Excess alcohol is then removed at reduced pressures until a thick syrup is formed. The syrup is used directly or is further processed to polyimide powder precursors which can be stored at room temperature over extended periods of time.

Graphite and/or other fibers and fillers can be added to the resulting composition to impart mechanical strength to the resulting foamed product. In order to control the pore size and/or the cellular structure of the foam, silicone based surfactants have also been included.

The viscous syrup or the solid resin is then converted to the copolyimide foam by heating it to 230 - 315°C for about 15 to 30 minutes. The foam resulting from the heating of the resinoid precursor is compressed by applying a pressure of 3 -20 psi in a preheated mold at 315°C. This process is continued until a permanent set of the foam is achieved.

This process has been used to produce polyimide foams that are resilient and flexible to rigid foams by varying the structure of the monomers used for polyimide synthesis. This flexible resilient foam has been obtained by using the diester diacid of benzophenone tetracarboxylic dianhydride (BTDA), 60 mole % of 4,4 - diamino diphenyl sulphone and 40 mole % of 2,6 diaminopyridine. The resilient foam was observed to have

hydrolytic stability.¹⁹⁰

Foaming the solid resin powder through direct thermal heating in a convection oven resulted in foams having irregular cellular structure with large cavities, due to the non-homogenous heat transfer through the thermally insulating polyimide foam. Therefore, indirect foaming methods such as dielectric heating and microwave heating have also been studied.

In the dielectric process, the electrical energy conversion to heat takes place almost instantaneously throughout the mass of the material and, therefore, the heating effect is usually very rapid. However, the cellular structure of the foam was irregular. On the other hand, foams produced via the microwave process were observed to be uniform and homogeneous. The resulting foamed material was devoid of any voids or imperfections. Foaming via the microwave process has also been highly reproducible in nature. Thus, by using the poly(amic alkyl ester) precursor, very low density polyimide foams have been developed via the microwave approach, by Gagliani and Supkis. These foams were found to be flexible with very homogeneous cell structure and excellent fire resistance, containing both open and closed cells.

2.10.4. Foams by the formation of the polyimide from the diisocyanate-dianhydride route

An alternative route to foaming polyimides is via the reaction of an isocyanate and an anhydride with the evolution of carbon dioxide, as described earlier. The carbon dioxide generated in this reaction has been used as the blowing agent to generate polyimide foams.

In this method, the reaction mixture is prepared from the starting anhydride and isocyanate. In one mode, these materials are mixed together in molten state at a temperature

of about 80 to 100°C without any added solvent. In another mode, a liquid solvent, such as DMSO, is used to dissolve the reactants. This results in the initial addition of the isocyanate to the anhydride, resulting in the formation of a seven membered cyclic isocyanurate structure. This rapidly breaks down with the elimination of carbon dioxide gas to form the imide linkage. Only low molecular weight polyimide materials are formed via this process. The resulting solid is later transferred to a mold and heated to about 200 to 250°C to further react, which releases more carbon dioxide, thus causing the polyimide to foam. The dianhydride-diisocyanate reaction product results in a rigid, hard foam body that is generally infusible.

In order for the dianhydride-diisocyanate reaction to proceed efficiently, water and a tertiary amine catalyst are included in the formulation. Addition of water has been observed by Carleton et al. to increase the rate of the dianhydride-diisocyanate reaction.¹⁹¹ They suggested the water hydrolyzes the isocyanate to urea, which reacts with the anhydride to form the imide. However Alvino and Edelman have shown that water is needed to open up the anhydride ring to a diacid moiety, and it is the reaction between the diacid and diisocyanate that increases the rate.¹⁹² Model reactions have indicated that the reaction between isocyanate and anhydride and/or acids yield both imide and amide products. Neither high temperature nor long reaction times are needed to obtain up to 50% yields of the amide or imide products. At temperatures $\leq 160^\circ\text{C}$, only about 70% of CO_2 was evolved and 100% CO_2 evolution was not obtained until a temperature of 200°C was reached.

Tertiary amine catalyst, such as triethyl amine, triethylene diamine, N,N,N',N'-tetramethyl-1-3-butanediamine and various other azacyclic compounds including N,N'-dialkyl piperazines, have been used to promote the reaction of the diisocyanate and the dianhydride and/or diacid. The preferred catalyst seems to be an alkanol amine, such as 1-hydroxyethynol-2-heptadecenyl glyoxalidine, triethanolamine or dimethyl ethanolamine.

The alkanol amine is added to the reaction mixture in catalytic amounts which range from 0.1 to 10% by weight of the reactants. The addition of alkanolamine allows the reaction to be conducted at lower temperatures with greater ease and control in processing. These catalysts improve the cell quality, friability and resiliency of the foamed product.¹⁹³

In order to further improve the foam cells structure, poly(siloxane) surfactants such as poly(siloxane) - poly(glycol) graft copolymers have been added in 2% to 40% by weight. The addition of siloxane-glycol copolymers as surfactants catalyze the isocyanate-carboxylic acid reaction, and produces foams with better flame resistance, cell quality and resilience.¹⁹⁴

Farrissey and coworkers¹⁹⁵ utilized the same type of polyisocyanate-dianhydride reaction to make crosslinked polyimide foams. Crosslinking was introduced by adding a highly functional polyol to react with part of the isocyanate so that the foam contained some urethane structure. A solvent and surfactant were included. Crosslinkable polyimide foams have also been developed by D'Allelo, endcapped the polyimide with monoamine containing terminal groups such as $-CH = CHR$, $-CN$, $-CHO$, $-CH = NR$ and ethynyl groups.¹⁹⁶

Various properties of polyimide foams obtained from polyisocyanate - benzophenone tetracarboxylic dianhydride by Farrissey et.al. is provided in Table 2.10.1.

The excellent thermal stability and fire resistant properties of this foam is apparent. Samples held at 232°C in air for 14 days were observed to suffer weight losses of less than 2% with no loss of compressive strength. A 6% weight loss was measured after 10 minutes at 450°C. Foam have also been prepared in a range of densities (2.5 to 18.5 lb / ft³) and compressive strengths (25 - 1340 psi).

2.11 APPLICATIONS FOR POLYIMIDE FOAMS

Application of these materials appears to offer the greatest pay-off when their high

temperature structural properties are used in conjunction with their insulative, ablative, and electrical properties. While these factors are interrelated, they are discussed separately in the following section¹⁹⁷

2.11.1. Insulative

Inherent thermal stability, high glass transition temperature coupled with low thermal conductivity results in excellent insulative properties. The ability of these materials to foam in place coupled with resistance of solvents such as aircraft fluids, and their inherent inflammability makes these materials highly attractive.

2.11.2. Ablative

The inflammability of polyimide foams and their low mass erosion ablative characteristics makes them attractive for use in manned reentry environment in hypersonic flight vehicles and lifting body reentry vehicles. Honeycomb structures made of these polyimide foams have also been tried as heat shield materials.

2.11.3. Structural

Honeycomb structures of polyimide foams have also been used for inserts, attachments and other connected load points.

2.11.4. Electrical

A low dielectric constant and low dielectric loss makes foamed polyimide materials good candidates for microwave windows. In addition, their low dielectric constant are useful in the area of multiple frequency or broad band windows. This, added to their excellent thermal stability and the insulating nature, makes it possible for these materials to be used more broadly. Polyimide foams have also been used in the area of radomes and in hypersonic missile radomes.

Table 2.10.1. Properties of Polyimide Foams from Polyisocyanate - Benzophenone tetracarboxylic diandhydride System (from ref. ¹⁹⁶)

Density, lb/ft ³	3.97
K-Factor (open cell), Btu/(h)(ft ²)(°F/in)	0.26
Compressive Strength, psi	
a) Parallel	34.9
b) Perpendicular	45.6
ASTM E84, Tunnel test - Flame Spreading Rate	10

3.0 - EXPERIMENTAL

3.1 PURIFICATION OF REAGENTS & SOLVENTS

All glassware, Teflon coated magnetic stir bars, overhead stir shaft, Teflon paddles, glass stir bars and syringes were scrupulously cleaned by washing with soap and water followed by rinses with acetone and/or tetrahydrofuran (THF). The equipment was allowed to air dry before being placed in a forced air convection oven for several hours. Syringes and needles were kept in the oven for several hours. For performing group transfer polymerization, the dried round-bottom flask and other glassware were equipped with an appropriate stir bar and the openings in the glassware were sealed with rubber septa. The septa were secured to the openings by wrapping twice with copper wire to insure a tight seal. Nitrogen flow through the apparatus was achieved by piercing the septa with a needle connected to a line with a flow of dry nitrogen. A purge needle was used to obtain nitrogen flow. The apparatus was then flame-dried using a Bunsen burner for several minutes and allowed to cool under dry nitrogen flow. When cool to the touch, the purge needle was removed and the apparatus were pressurized with dry nitrogen. Syringes, upon removal from the oven, were purged with dry nitrogen and allowed to cool in a desiccator shortly before use. Immediately prior to use, the syringes were again purged with dry nitrogen. All transfers of the monomers and solvent for the reaction were transferred either using cannula or syringe techniques.

In order to synthesize imide containing polymers and copolymers of high molecular weight and controlled composition, it was necessary to obtain pure starting materials and to maintain anhydrous conditions thorough out the synthetic processes. For these reasons, reagents and monomers were carefully purified by various techniques, and polymerization solvents were distilled from drying agents using standard distillation apparatus. All distilled solvents were collected in a round bottom flask sealed with a rubber septum and

stored under nitrogen. The dried solvents were generally handled using syringe techniques to minimize atmospheric exposure.

3.1.1 SOLVENT PURIFICATION

3.1.1.1 Acetic Anhydride (Ac₂O, Aldrich) was used as received as a cosolvent in the chemical imidization step of the polyimide synthesis. (BP 138-140°C/760mm)

3.1.1.2 Ethyl acetate (EtOAc, Aldrich) was used as received in the synthesis of the meta and para diacyl chloride diester of PMDA. (BP. 76 77°C/760mm)

3.1.1.3 1-Methyl-2-Pyrrolidinone (NMP, Fisher) was dried over P₂O₅ for at least 8 hours under nitrogen and then distilled at 85°C under reduced pressure of 500 mtorr just prior to use. NMP was used as solvent for polyimide synthesis. (BP. 205°C/760 mm)

3.1.1.4 Methanol (CH₃OH, Fisher, HPLC Grade) was used as a terminating agent for the group transfer polymerization's. It was stored in a septum sealed storage bottle and was thoroughly degassed prior to use by sparging with dry nitrogen for ca. 30 minutes.

3.1.1.5 Pyridine (Py, Aldrich) was used both as an acid acceptor during the end functionalization step of the mono hydroxy oligomers and as a cosolvent in the chemical imidization step of the polyimide synthesis. It was dried over calcium hydride under nitrogen for at least 8 hours and then distilled at 100 °C under reduced pressure of 500 mtorr just prior to use.(BP 115°C/760mm)

3.1.1.6 Tetrahydrofuran (THF, Fisher) was used for both group transfer polymerization of methyl methacrylate and for poly(amic alkyl ester) synthesis. It was

placed in a 1L or 2L one necked round-bottom flask equipped with a magnetic stirrer. A paraffin wax dispersion of sodium (50% by wt., Aldrich) was then added and the solvent was degassed by spurring with dry nitrogen for 30 minutes. The flask was fitted to a solvent still and allowed to reflux for at least 24 hours under static atmosphere of dry nitrogen. A small amount of benzophenone (Aldrich) was then added to the THF/Sodium mixture. The appearance of a deep purple color with the sodium/benzophenone ketyl indicated that the solvent was ready for use. The THF was freshly distilled prior to use at atmospheric pressure under nitrogen atmosphere. (bp 76°C/760mm)

3.1.1.7 Deuterated Chloroform (CDCl₃, Aldrich) was used as an N. M. R. solvent for poly(methyl methacrylate) and polyimides. It was dried over molecular sieves for at least 24 hours and was not distilled prior to use. (bp 61°C/760 mm)

3.1.1.8 Deuterated Dimethyl Sulfoxide (DMSO-d₆, Aldrich) was also used as n. m. r. solvent for polyimides. It was dried over molecular sieves for at least 24 hours and was not distilled prior to use. (bp 55°C/5 mm)

3.1.2 MONOMERS, CATALYSTS AND REAGENTS

3.1.2.1 3-Aminophenyl acetylene

Supplier: Eastman Kodak

Molecular Formula: C₈H₇N

Molecular Weight, g/mole: 117.12

Purification: 3-aminophenyl acetylene was purified by distillation under reduced pressure

3.1.2.2 Benzoic acid

Supplier:	Aldrich
Molecular Formula:	C ₇ H ₆ O ₂
Molecular Weight, g/mole:	122.12
Melting Point(Pure), °C	122-123°C

Purification: Benzoic acid was used as received in the synthesis of the catalyst for the group transfer polymerization of methyl methacrylate.

3.1.2.3 3,3',4,4'-Benzophenonetetracarboxylic dianhydride(BTDA)

Supplier:	Eastman Kodak
Molecular Formula:	C ₁₇ H ₆ O ₇
Molecular Weight, g/mole:	322.23
Melting Point(Pure), °C	224-226°C

Purification: Polymer grade BTDA was used after drying at 180°C for at least 6 hours to obtain high molecular weight polyimides.

3.1.2.4 3,3',4,4'-biphenyltetracarboxylic dianhydride(BPDA)

Supplier:	Chourishev
Molecular Formula:	C ₁₆ H ₆ O ₆
Molecular Weight, g/mole:	294
Melting Point(Pure), °C	300

Purification: Polymer grade BPDA was used after drying at 180°C for at least 6 hours to obtain high molecular weight polyimides.

3.1.2.5 4-t-Butylphthalic Anhydride(t-butyl PA)

Supplier:	TCI
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Molecular Formula: $C_{12}H_{12}O_3$

Molecular Weight, g/mole: 204.23

Melting Point(Pure), $^{\circ}C$ 78

Purification: PA was sublimed under vacuum at a temperature of $125^{\circ}C$.

3.1.2.6 3,5-dinitrobenzoyl chloride

Supplier: Aldrich

Molecular Formula: $C_7H_3O_5N_2Cl$

Molecular Weight, g/mole: 230.56

Melting Point(Pure), $^{\circ}C$ 50-52

Purification: The compound was purified by distillation at $85^{\circ}C$ under reduced pressure of about 300 mtorr.

3.1.2.7 5,5'-[2,2,2-Trifluoro-1-(trifluoromethyl) ethylidene] bis-1,3-isobenzofurandinone (6FDA)

Supplier: Hoechst Celanese Corporation

Molecular Formula: $C_{19}H_6F_6O_6$

Molecular Weight, g/mole: 444

Melting Point(Pure), $^{\circ}C$ 247

Purification: Polymer grade 6FDA was used after drying at $180^{\circ}C$ for at least 6 hours to obtain high molecular weight polyimides.

3.1.2.8 Methyl Methacrylate

Supplier: Aldrich

Molecular Formula: $C_5H_8O_2$

Molecular Weight, g/mole: 100.12

Melting Point(Pure),°C - 48

Purification: MMA was purified by transferring the desired amount of monomer into the left side of the flame dried, bulb-to-bulb distillation apparatus equipped with a stir bar. Finely divided calcium hydride was added and a ground glass stopcock sealed with a rubber septum that was secured with copper wire was attached to the glass joint above the monomer. The mixture was stirred for 24 hours after which the monomer was cooled by placing a dry ice/isopropanol bath around the side of the apparatus containing the monomer. After the monomer had sufficiently cooled, vacuum was applied to the apparatus via the three-way stopcock on the right hand side and the distillation apparatus was flame-dried beginning at the cross path directly above the monomer and proceeding to the right. Once the glassware had cooled sufficiently, all joints were secured with rubber bands to allow the system to be pressurized with dry nitrogen without leaks. The system was pressurized with dry nitrogen and a purge needle was placed thorough the septum to allow the apparatus to cool under nitrogen flow. The monomer was then thoroughly degassed by several freeze/flame/thaw cycles as previously described. The monomer was distilled by vacuum bulb to bulb transfer from left hand side to the dry ice /isopropanol cooled receiver side. The calcium hydride dried monomers were then transferred via cannula into doubly septum sealed, flame-dried bottles and stored in freezer under nitrogen.

Just before the polymerization reaction, distilled MMA monomer was further purified by transferring from the storage bottle to a flame-dried bulb-to-bulb distillation apparatus. After several freeze/flame/thaw cycles, triethyl aluminum (Ethyl Corporation, 25wt% in hexane) was added dropwise via syringe to the cold monomer. Upon addition of a sufficient amount of the triethyl aluminum solution, a faint yellow-green color became apparent indicating quenching of all protic impurities by triethyl aluminium in the monomer. The monomer was protected from light by wrapping the container with

aluminum foil and the monomer/complex solution was warmed to room temperature and distilled bulb-to-bulb using vacuum as described earlier. The monomer was kept in the receiver bulb at -78°C , protected from light until 10 minutes before use. At that time, the monomer was allowed to warm up to room temperature and transferred to the polymerization reactor via syringe.

3.1.2.9 4-nitrobenzoyl chloride

Supplier:	Aldrich
Molecular Formula:	$\text{C}_7\text{H}_4\text{O}_3\text{NCl}$
Molecular Weight, g/mole:	185.57
Melting Point(Pure), $^{\circ}\text{C}$	25

Purification: The compound was purified by distillation at 60°C under reduced pressure of about 300 mtorr.

3.1.2.10 Oxalyl chloride

Supplier:	Aldrich
Molecular Formula:	$\text{C}_2\text{O}_2\text{Cl}_2$
Molecular Weight, g/mole:	126.93
Boiling Point(Pure), $^{\circ}\text{C}$	$63-64^{\circ}\text{C}/763\text{ mm}$

Purification: Oxalyl chloride was used as received in the synthesis of meta and para diacyl chloride diester of PMDA.

3.1.2.11 4,4'-oxydiphthalic anhydride (ODPA)

Supplier:	Occidental Chemical Corporation
Molecular Formula:	$\text{C}_{16}\text{H}_6\text{O}_7$
Molecular Weight, g/mole:	310.23

Melting Point(Pure), °C 228

Purification: Polymer grade ODPAA was used after drying at 180°C for at least 6 hours to obtain high molecular weight polyimides.

3.1.2.12 Palladium hydroxide/carbon (Pearlman's catalyst)

Supplier: Aldrich

Molecular Formula: Pd(OH)₂/C

Purification: Pearlman's catalyst was used as received for the reduction of the nitro compounds to amino compounds.

3.1.2.13 Propylene Oxide (PO)

Supplier: ARCO Chemical Company

Molecular Formula: C₃H₆O

Molecular Weight, g/mole: 58

Boiling Point(Pure), °C 34

Purification: PO was purified by distillation over calcium hydride under atmospheric pressure.

3.1.2.14 Pyromellitic dianhydride (PMDA)

Supplier: Allco

Molecular Formula: C₁₀H₂O₆

Molecular Weight, g/mole: 218.12

Melting Point(Pure), °C 286

Purification: Polymer grade PMDA was obtained by subliming the compounds three times over neutral alumina at 225°C under reduced pressure.

3.1.2.14 Stannous chloride

Supplier:	Aldrich
Molecular Formula:	$\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$
Molecular Weight, g/mole:	225.63
Melting Point(Pure), °C	37.7

Purification: The catalyst was used as received for the reduction of nitro compounds to amino compounds.

3.1.2.15 Tetrabutylammonium hydroxide

Supplier:	Aldrich
Molecular Formula:	$\text{C}_{16}\text{H}_{37}\text{NO}$
Molecular Weight, g/mole:	259.48

Purification: The compound was used as received for the synthesis of the catalyst for group transfer polymerization of methyl methacrylate.

3.1.2.16 2,2,2-Trifluoroacetophenone

Supplier:	Aldrich
Molecular Formula:	$\text{C}_8\text{H}_5\text{F}_3\text{O}$
Molecular Weight, g/mole:	172.12
Boiling Point(Pure), °C	165

Purification: The compound was distilled under reduced pressure using a vacuum puMP

3.1.2.17 1,1-bis(4-aminophenyl)-1-(4-ethynylphenyl)-2,2,2-trifluoroethane (EDA)

Supplier:	IBM
Molecular Formula:	$\text{C}_{12}\text{H}_{17}\text{F}_3\text{N}_2$
Molecular Weight, g/mole:	366

Melting Point(Pure),°C 161-163

Purification: The compound was synthesized using the procedure reported by Jensen and Hergenrother.¹⁹⁸ The material was used as received.

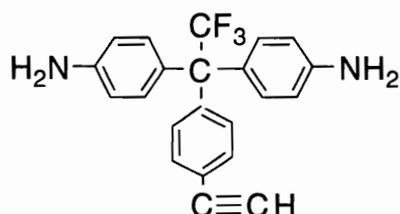


Figure 3.1.2.1 1,1-bis(4-aminophenyl)-1-(4-ethynylphenyl)-2,2,2-trifluoroethane (EDA)

3.2 SYNTHESIS OF MONOMERS, CATALYST AND INITIATOR

3.2.1 SYNTHESIS OF MONOMERS

3.2.1.1 Synthesis of 1,1-Bis(4-Aminophenyl)-1-Phenyl-2,2,2-Trifluoroethane(3FDA)

The synthesis of 3FDA is depicted in Figure 3.2.1.1. In a typical experiment, a 1-L, three necked round bottom flask equipped with a stir bar, thermocouple, Ar inlet and Dean-Stark condenser was added 54.6 g (0.287 mol) p-toluenesulfonic acid monohydrate and 325 mL of freshly distilled aniline and the mixture refluxed to a constant head temperature (184°C) with separation of water. The Dean-Stark trap was replaced by a regular condenser while the pot temperature was reduced to 130°C under positive Ar pressure. At this point, 50.0 g(0.287 mol) of 2,2,2-trifluoroacetophenone was added in one portion and the mixture heated at 145°C with stirring for 48 hours. The reaction mixture was then cooled to 90°C and 500 mL of 1N NaOH was added in one portion with vigorous stirring and the layers separated. After cooling to room temperature, 1-L of CH₂Cl₂ was added while stirring and the layers separated. The aqueous layer was extracted with 150 mL of CH₂Cl₂ and the combined organic layers washed sequentially with 4 * 250 mL of

sat. NaHCO_3 , 4 * 250 mL of water and 200 mL of brine. The dark solution was dried over MgSO_4 , evaporated to approximately 300 mL and added slowly to 4L of stirring hexane. The hexane was decanted and the resulting dark semi-solid was taken up in about 500 mL of CH_2Cl_2 , which was again reduced to approximately 300 mL and added slowly to 4 L of stirring hexane. The suspension was filtered to yield 78 g of a purple-red solid which was in turn dissolved in 2 L of diethyl ether and treated with 500 g of silica gel (60-230 mesh) and 100 g of Norit with stirring overnight. The mixture was filtered over Celite, the filtrate concentrated to approximately 125 mL and the product slowly precipitated with stirring into 2 L of hexane. This procedure (re suspension of the original SiO_2 /Norit, stirring for 1 hour, filtration and precipitation) was repeated a total of 4 times resulting in a total of 68 g of beige powder (subsequent treatments provided exceedingly small amounts of material). This material was taken up in 1 L of diethyl ether and treated with 50 g of silica gel and 5 g of Norit. Processed as above with precipitation into 1 L of hexane ultimately resulted in 63 g of white powder, mp 215 - 218°C (lit mp 218 - 220°C).¹⁹⁹ Finally, the diamine was recrystallized from 95% ethanol/water mixture by adding the diamine to the ethanol at a 1 to 9 ratio by weight. The mixture was heated until the diamine dissolved and then water was slowly added until the solution became cloudy at which point the solution was cooled below 0°C to obtain off-white crystals. The crystals were filtered and dried at 110°C in a vacuum oven resulting in 53 g of the diamine monomer. Yield 54%. NMR(ppm) 7.26 (m, 3H, phenyl), 7.2 (m, 2H, phenyl), 6.92 (d, 4H, aniline), 6.61 (d, 4H, aniline), 3.70 (s, 4H, NH_2).

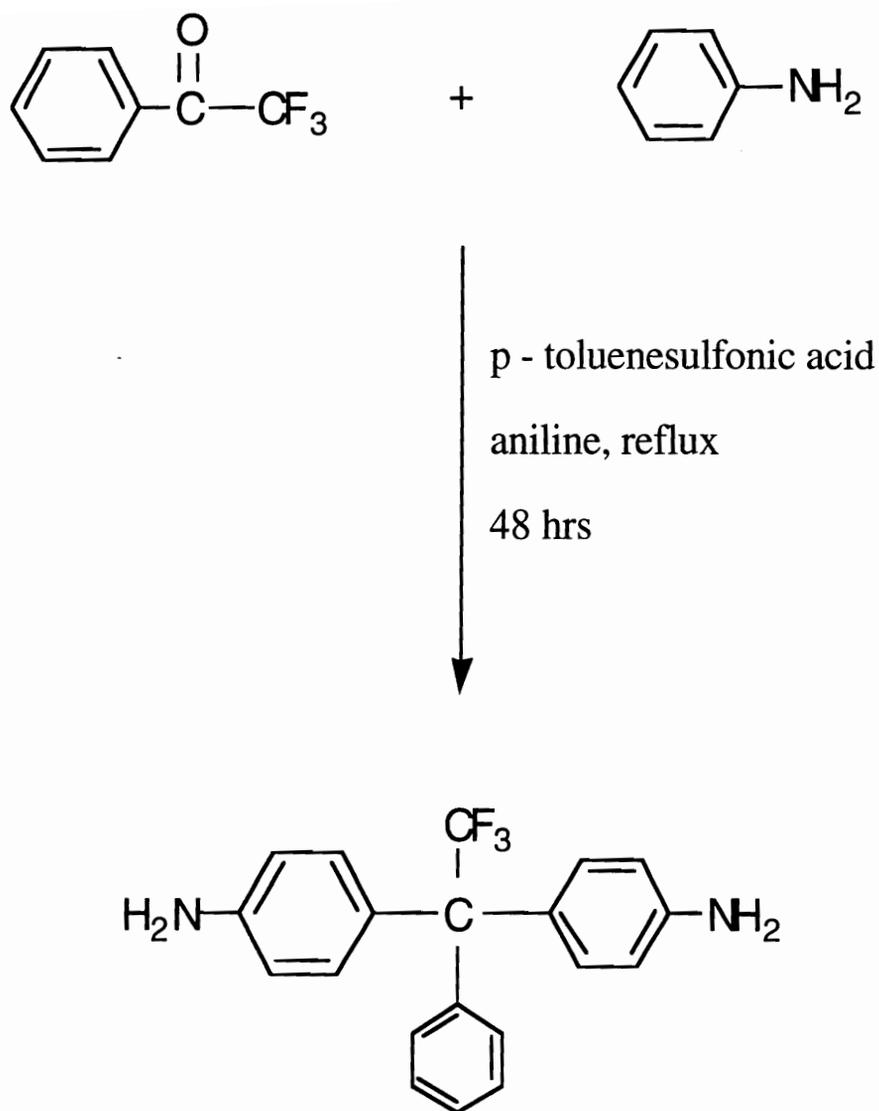


Figure 3.2.1.1 Synthesis of 1, 1-bis(4-aminophenyl)-1-phenyl-2,2,2-trifluoroethane (3FDA)

3.2.1.3 Synthesis of meta and para-Diacid Diethyl Pyromellitate (m/p-diacid diester of PMDA)

The synthesis of diacid diethyl pyromellitate is depicted in Figure 3.2.1.2. It was synthesized using a procedure reported by Bell and Jewell.^{ref} In a typical experiment, a 250 mL three necked round bottom flask equipped with a stir bar, reflux condenser, and an Ar inlet, were added 52.3 g (0.24 moles) of pyromellitic dianhydride (PMDA) and dry ethanol (150 mL). The reaction mixture was heated gently and allowed to reflux for 4 hours. The heating was stopped and 50 mL of ethyl acetate was added and the reaction mixture was allowed to stir overnight at room temperature. A white crystalline solid (crop 1) that resulted was filtered and washed twice with 25 mL of ethyl acetate. The filtrate and the wash were combined and slowly evaporated at reduced pressure until turbidity ensued. The suspension was heated to dissolution and allowed to cool slowly to room temperature with stirring. The resulting white solid was filtered off (crop 2), washed once with 15 mL of ethyl acetate, filtrate and washing were combined and then treated as before. The white, crystalline precipitate was filtered (crop 3) and washed with 15 mL of 1:1 ethyl acetate/hexane mixture and finally 15 mL of hexane. The filtrate and washings were once again combined and treated as before. The resulting slurry was filtered (crop 4) and washed with 15 mL of hexane. The remaining filtrate was discarded. All crops were dried in a vacuum oven separately at 50°C. ¹H NMR analysis of the individual crops reveal that crops 1 and 2 were primarily the para diacid diester and crops 3 and 4 were primarily the m-isomer. Pure meta and para isomers were prepared by recrystallization of the respective crops in hexane/ethyl acetate mixture. Combined yield 71.9 g (96.3%) [meta / para ratio 37.5 g (51.8%) / 34.4 g (47.8%)].

3.2.1.4 Synthesis of para-Diacyl Chloride Diethyl Pyromellitate (p-diacidchloride diester of PMDA)

The para-diacid diethyl pyromellitate obtained from crop 1 and 2 were converted to the p-diacylchloride diester derivative by treating with oxalyl chloride. In a typical experiment 25 g of the para-diacid diethylester derivative of PMDA (0.075 mol) and ethyl acetate(100 mL) were added to a 250 mL flask equipped with a stirrer, a reflux condenser, an Ar inlet and an addition funnel. The reaction mixture was heated to 60°C and 27.3 g of oxalyl chloride (0.215 mol) was added over a period of 3 - 4 hours. The temperature was maintained between 55-60°C for about 12 hours. The reaction mixture was cooled and excess oxalyl chloride along with ethyl acetate was stripped off using vacuum distillation (35-55°C at 26" Hg). The oily product that was obtained was crystallized and recrystallized from hexane to yield 21 g of p-diacylchloride diethylester of PMDA as a white crystalline solid, mp 87-88°C (Lit MP 88 - 90°C)⁸⁵. Yield 80%.

3.2.1.5 Synthesis of meta-Dichloro Diethyl Pyromellitate (m-diacylchloride diester of PMDA)

The pure meta-diacid diethyl pyromellitate obtained from crop 3 and 4 was converted to the m-diacylchloride diester derivative by treating with oxalyl chloride. In a typical experiment 23.3 g of the m-diacid diethylester derivative of PMDA (0.075 mol) and ethyl acetate (100 mL) were added to a 250 mL flask equipped with a stirrer, a reflux condenser, an Ar inlet and an addition funnel. The reaction mixture was heated to 55-60°C and 30 g of oxalyl chloride(0.236 mol) was added over a period of 3-4 hours. The temperature was maintained between 55-60°C for about 12 hours. The reaction mixture was cooled and excess oxalyl chloride along with ethyl acetate was stripped off using vacuum distillation. The oily product that was obtained was crystallized and recrystallized

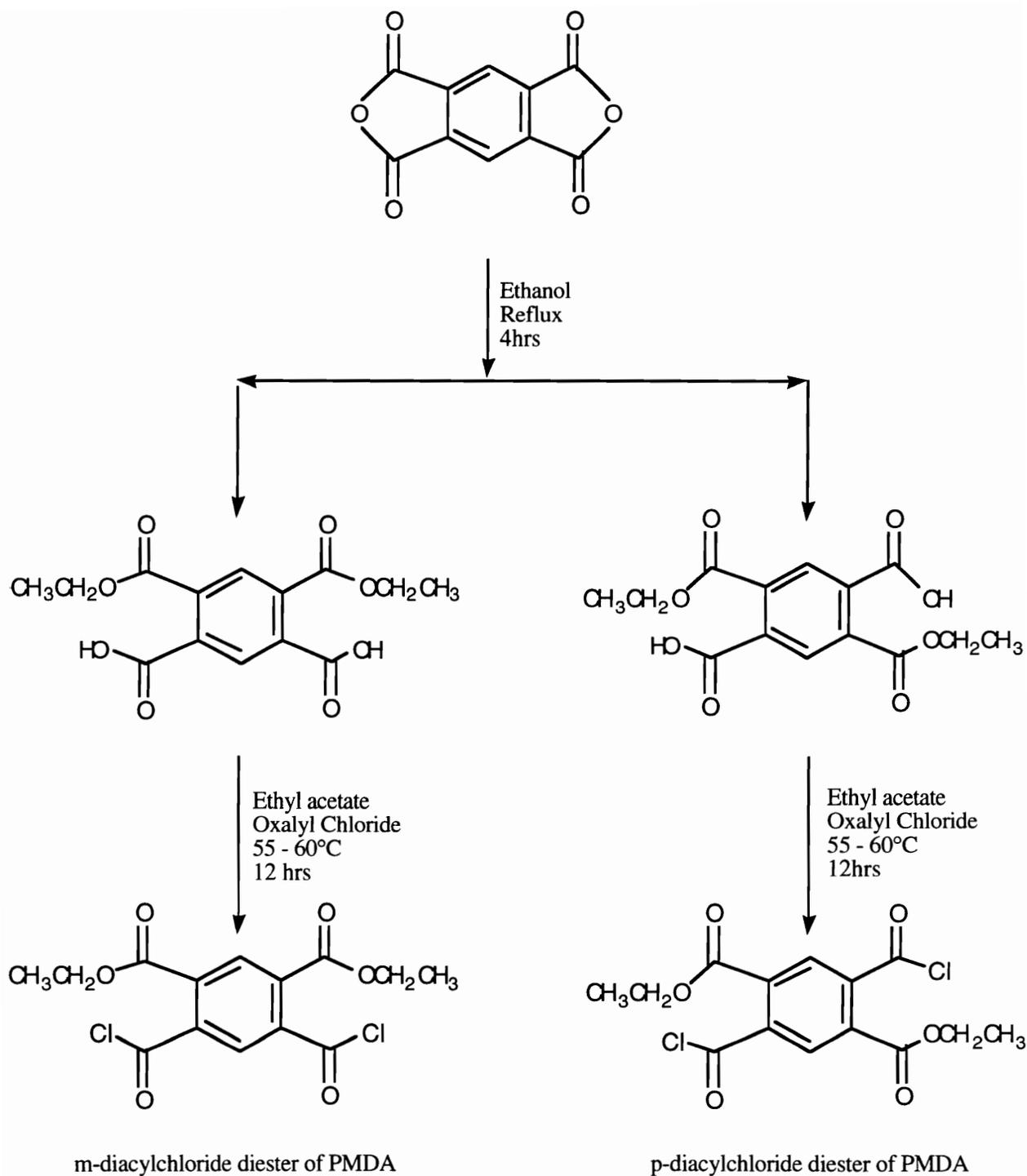


Figure 3.2.1.2 Synthesis of para-dichloro diethyl pyromellitate (p-diacylchloride diester of PMDA) and meta-dichloro diethyl pyromellitate (m-diacylchloride diester of PMDA).

from hexane to yield 17.6 g of m-diacylchloride diethylester of PMDA as a white crystalline solid, MP 53 - 55°C (Lit MP 54 -56°C).⁸⁵ Yield 69%.

3.2.1.6 Synthesis of 2-(Trimethylsilyloxy)Ethyl (Trimethylsilyl) Dimethylketene Acetal

The initiator 2-(trimethylsilyloxy)ethyl (trimethylsilyl) dimethylketene acetal for the group transfer polymerization of MMA was synthesized and purified as reported by Lutsenko et al.²⁰⁰ This was synthesized from purified 2-hydroxyethyl methacrylate (HEMA). Silylation of the hydroxy functional group proceeded through the addition of trimethylchlorosilane to 2-hydroxyethyl methacrylate. The reaction was carried out in tetrahydrofuran (THF) at 0°C with triethylamine as the acid acceptor. After the reaction the triethylamine hydrochloride salts were removed through filtration and the 2-(trimethylsilyloxy)ethyl methacrylate was distilled prior to hydrosilylation. 0.1 mole% (based on methacrylate) of Wilkinson's catalyst was charged to a dry reaction vessel and the flask was subsequently pressurized with 6-8 psi of nitrogen. The protected methacrylate was charged to the flask followed by the slow addition of dimethylethylsilane. The hydrosilylation reaction proceeded for ca. 16 hours at 50°C under a nitrogen atmosphere affording a silyl ketene acetal hydroxy functional initiator. Both silylation of the hydroxy functional group and hydrosilylation forming the ketene silyl acetal were monitored using ¹H NMR and FTIR.

3.2.1.7 Synthesis of tetrabutylammonium benzoate (TBAB)

TBAB, the catalyst used in group transfer polymerization's, was prepared from purified benzoic acid(Aldrich) and tetrabutylammonium hydroxide, a 40 weight percent in water (Aldrich).²⁰¹ A 1:1 stoichiometric ratio of the two reagents were vigorously mixed in a separatory funnel. A slight exotherm was evident, and once the solution returned to

room temperature, the aqueous solution was extracted three times with 25 mL aliquots of methylene chloride. The methylene chloride layer, which contained the TBAB, was dried by vigorous stirring over anhydrous magnesium sulfate for several minutes followed by filtration to remove the drying agent. The methylene chloride was removed in vacuum and the remaining solid was dissolved in warm tetrahydrofuran. The volume of THF was reduced by using a rotary evaporator until the formation of crystals became evident. At this point, dry diethyl ether was added to the solution to facilitate crystal growth. The crystals formed were filtered and washed with diethyl ether and dried under vacuum at room temperature. TBAB was stored in a brown glass bottle that was capped, sealed with parafilm and stored in a sealed jar containing activated drierite until use.

3.3 SYNTHESIS OF MACROMONOMERS AND POLYMERS

3.3.1 Synthesis of Macromonomers

3.3.1.1 Mono Hydroxy Terminated Polypropylene Oxide ($M_n = 4000$ g/mole) Oligomer

The synthesis of mono hydroxy terminated polypropylene oxide is depicted in Figure 3.3.1.1. The synthesis of mono hydroxy terminated polypropylene oxide was achieved by the anionic ring opening polymerization of the propylene oxide monomer using a phenolate anion. In a typical experiment, a 250 mL three necked round bottom flask equipped with a stir bar, a Dean-Stark condenser, and an Ar inlet, was added 10 g (0.1063 mol) of phenol and 50 mL of dimethyl sulfoxide (DMSO). To this solution was added 14.69 g of K_2CO_3 (0.106 mol), along with 10 mL of toluene. Toluene was used to facilitate the azeotropic removal of water formed during the reaction. The reaction mixture was stirred for 5 hours at $135^\circ C$, during which the water formed was stripped off along with excess toluene. The entire solution containing the phenate ion was then transferred to a pressure reactor along with 50 mL of freshly distilled THF. 425 g (7.73 mol) of freshly

distilled propylene oxide monomer was then charged into the reactor using a syringe. The temperature of the reaction mixture was observed to raise immediately indicating the onset of polymerization. The polymerization was allowed to proceed for a minimum of 48 hours at 60°C after which the reaction was terminated by adding a large excess of methanol. Methanol and all unreacted propylene oxide monomer were stripped off under reduced pressure, which resulted in a light yellow viscous oil. The viscous oil was dissolved in hexanes and treated with 2 g of Norit. The mixture was filtered over celite and the filtrate was removed using a rotovap to obtain 125 g of colorless viscous polymer. Similar procedure was used to synthesize other mono hydroxy polypropylene oxide oligomers whose number average molecular weight ranged from 2000 g/mole to 8000g/mole.

3.3.1.2 Monofunctional 4-Aminobenzoate terminated polypropylene oxide macromonomer

The general procedure for the functionalization of PO oligomers with 4-aminobenzoate end group is given for 5K oligomer and is also depicted in Figure 3.3.1.1. To a two necked, 100 mL, round bottom flask equipped with a stir bar, argon inlet and a condenser was added 25 g (5 mmol) of monofunctional hydroxy propylene oxide oligomer of molecular weight 5000 g/mole. To this 2 g (0.025 mole) pyridine was added, followed by 150 mL of freshly distilled tetrahydrofuran (THF). The mixture was cooled in ice and to this, 4.64 g(0.025 mole) of 4-nitrobenzoyl chloride was added in one portion and the mixture stirred for 24 hours. The precipitated pyridinium hydrochloride salt was then filtered, washed with an additional 25 mL of THF, and the combined filtrates concentrated on a rotovap. The extent of end functionalization of PO oligomer was monitored using ^1H NMR. The amorphous residue was then redissolved in THF, 100 mg of Pd(OH)₂ on activated carbon was added and the mixture was catalytically hydrogenated in a Parr hydrogenator apparatus for about 48 hours at 50 psi hydrogen pressures. The

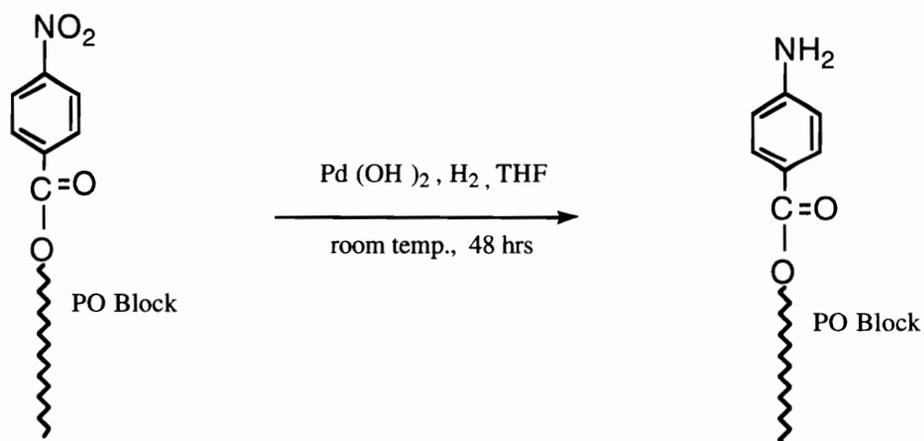
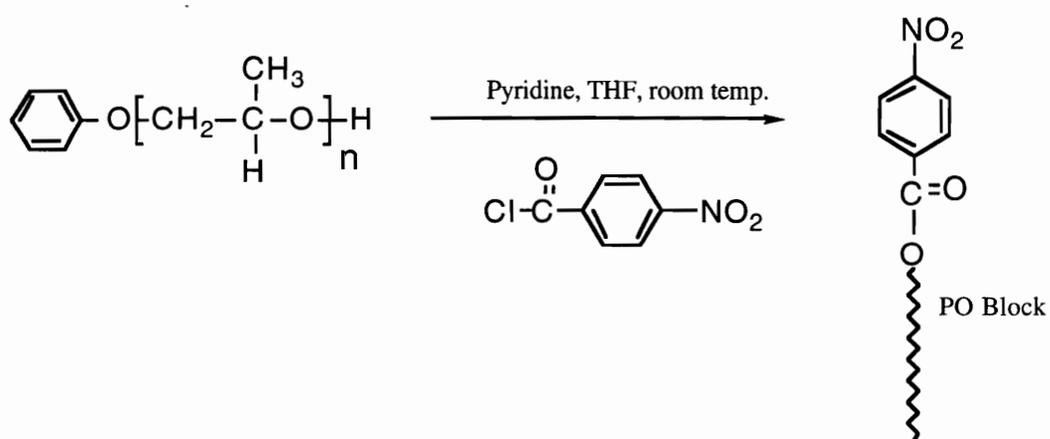
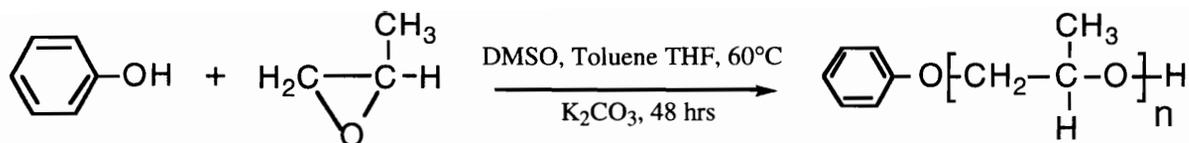


Figure 3.3.1.1 Synthesis of 4-aminobenzoate Terminated Polypropylene Oxide ($M_n = 4000$ g/mole) Oligomer

hydrogenated mixture was filtered through a bed of celite, treated with activated charcoal, filtered and the filtrate THF was removed using a rotovap. The resulting diamino derivative was azeotroped with toluene to facilitate drying. The excess toluene was then distilled from the flask and finally with a kugelrohr at 125°C (20 mm/Hg) to remove residual toluene. This yielded the monoamino terminated PO oligomer as clear liquids. The extent of reduction was confirmed using a ^1H NMR and thorough potentiometric titration of the amine, against HBr in acetic acid. The number average molecular weights of the oligomer was found to be 5600 g/mole.

3.3.1.3 3,5-Diaminobenzoate terminated polypropylene oxide macromonomer

The general procedure for the functionalization of PO oligomers with 3,5 - diamino benzoate end group is given for a 8K oligomer as depicted in Figure 3.3.1.2. To a two necked, 100 mL, round bottom flask equipped with a stir bar, argon inlet and a condenser was added 20 g (2.5 mmol) of monofunctional hydroxy PO oligomer of molecular weight 8000 g/mole. To this 980 mg (0.0125 mole) pyridine was added, followed by 150 mL of freshly distilled tetrahydrofuran (THF). The mixture was cooled in ice and to this 2.88 g(0.0125 mol) 3,5-dinitrobenzoyl chloride was added in one portion and the mixture stirred for 24 hours. The precipitated pyridinium hydrochloride salt was then filtered, washed with an additional 25 mL of THF, and the combined filtrates concentrated on a rotovap. The extent of end functionalization of PO oligomer was monitored using ^1H NMR. The amorphous residue was then redissolved in THF, 200 mg of Pd(OH)₂ on activated carbon was added and the mixture was catalytically hydrogenated in a Parr hydrogenator apparatus for about 48 hours at 50 psi hydrogen pressures. The hydrogenated mixture was filtered through a bed of celite and activated charcoal and the solution concentrated in a rotovap. The resulting diamino derivative was azeotroped with toluene to facilitate drying. The excess toluene was then distilled from the flask and finally with a kugelrohr at 125°C

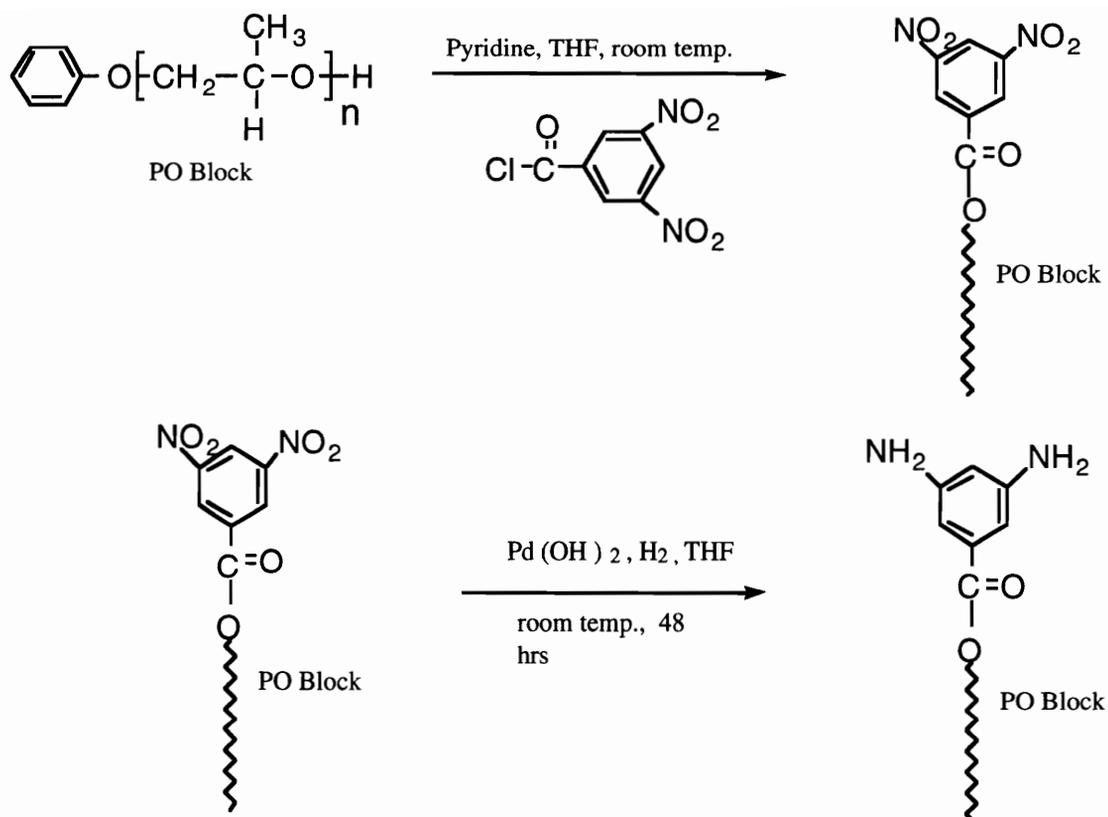


Figure 3.3.1.2 Synthesis of 3,5-diaminobenzoate terminated polypropylene oxide macromonomer

(20 mm) to remove residual toluene. This yielded the diamino-terminated PO oligomer as clear liquid. The extent of reduction was confirmed using a ^1H NMR and thoroughpotentiometric titration of the amine against HBr in acetic acid. The number average molecular weight of the oligomer was determined to be 7900 g/mole.

3.3.1.4 Mono Hydroxy Terminated Poly(methyl methacrylate)

Mono hydroxy terminated poly(methyl methacrylate) was synthesized using group transfer polymerization (GTP) of methyl methacrylate monomer with 2-(trimethylsilyloxy)ethyl (trimethylsilyl) dimethylketene acetal as the initiator and tetrabutylammonium benzoate as the catalyst at room temperature. A sample calculation of the amounts necessary to make 25 g of 5000 g/mole PMMA is shown in Figure 3.3.1.3. The synthetic procedure is depicted in Figure 3.3.1.4. All the GTP reactions were carried out in a clean, flame dried, single neck round bottom flask equipped with a Teflon coated magnetic stir bar and fitted with a wire secured rubber septum. In order to synthesize 25 g of polymer, a 500 mL flask was used, to which 350 mL of the freshly distilled polymerization solvent, THF was added via cannula. Small amount of THF solvent was also added to the vial containing the catalyst tetrabutylammonium benzoate, which had been dried overnight in the same septum sealed serum vial under high vacuum, typically 50-200 mtorr. In general, one mole percent based on the GTP initiator was used for all the reactions. All the catalyst was quantitatively transferred to the reaction vessel via cannula under a nitrogen atmosphere. To this reaction mixture was charged a calculated amount of the GTP initiator via syringe. The initiator and the catalyst solution was allowed to complex for approximately 10 minutes. In order to monitor the reaction exotherm a surface temperature probe was placed against the outside wall of the reaction flask. A calculated amount of freshly distilled triethylaluminium purified MMA was then added via syringe. To prevent the condensation of atmospheric moisture on the tip of the syringe needle, due

to MMA being cold upon removal from the distillation apparatus, the tip of the needle was covered with laboratory tissue while transferring. The rate of addition was maintained such that the reaction temperature was always below 20°C. Upon complete addition of the monomer into the reaction vessel, the reaction was allowed to proceed for another 2-3 hours, after which the reaction was terminated by adding 0.5-1.0 mL of HPLC grade methanol. A small aliquot of the polymer containing the trimethylsilyl protected terminal hydroxyl group was removed and precipitated into tenfold excess hexanes, filtered and dried for estimation of the molecular weight by ^1H NMR. The trimethylsilyl protecting group in the polymer was then cleaved in situ by addition of 0.5 - 1.0 mL of dilute methanolic HCl solution and stirring for several more hours. Approximately 50% of the solvent was removed by rotary evaporation under reduced pressure and the resulting polymer solution was then precipitated into a rapidly stirred 10 fold volume excess of hexanes. The polymer was filtered, washed with hexanes and dried in a vacuum oven at room temperature. The molecular weight of the oligomer was determined to be 7600 g/mole using ^1H NMR.

3.3.1.5 3,5-Diaminobenzoate terminated poly(methyl metacrylate) macromonomer

The general procedure for the functionalization of PMMA oligomers with 3,5-diamino benzoate end group is given for a 7600g/mole number average molecular weight oligomer and is also depicted in Figure 3.3.1.4. To a two necked, 100 mL, round bottom flask equipped with a stir bar, argon inlet and a condenser was added 10 g (1.43 mmol) of monofunctional hydroxy PMMA oligomer of molecular weight 7000 g/mole. To this 0.79 g (0.01 mol) pyridine was added, followed by 150 mL of freshly distilled tetrahydrofuran (THF). The mixture was cooled in ice and to this 2.3 g 3, 5-dinitro benzoyl chloride (0.01 moles) was added in one portion and the mixture stirred for 24 hours. The precipitated pyridinium hydrochloride salt was then filtered, washed with an additional 25 mL of THF,

$$\text{g (monomer) / density (monomer) = mL (monomer)}$$

$$\text{g (monomer) / mol. wt. (polymer) = moles (initiator)}$$

$$\{ \text{moles (initiator) X (g / mole) (initiator) } \} / (\text{g / mL}) (\text{initiator}) = \text{mL (initiator)}$$

$$\text{moles (initiator) X 0.1 \% = moles (catalyst)}$$

$$\text{moles (catalyst) X (g / mole) (catalyst) = g (catalyst)}$$

Figure 3.3.1.3 Sample calculations for the amounts of materials used in the synthesis of PMMA Via Group Transfer Polymerization

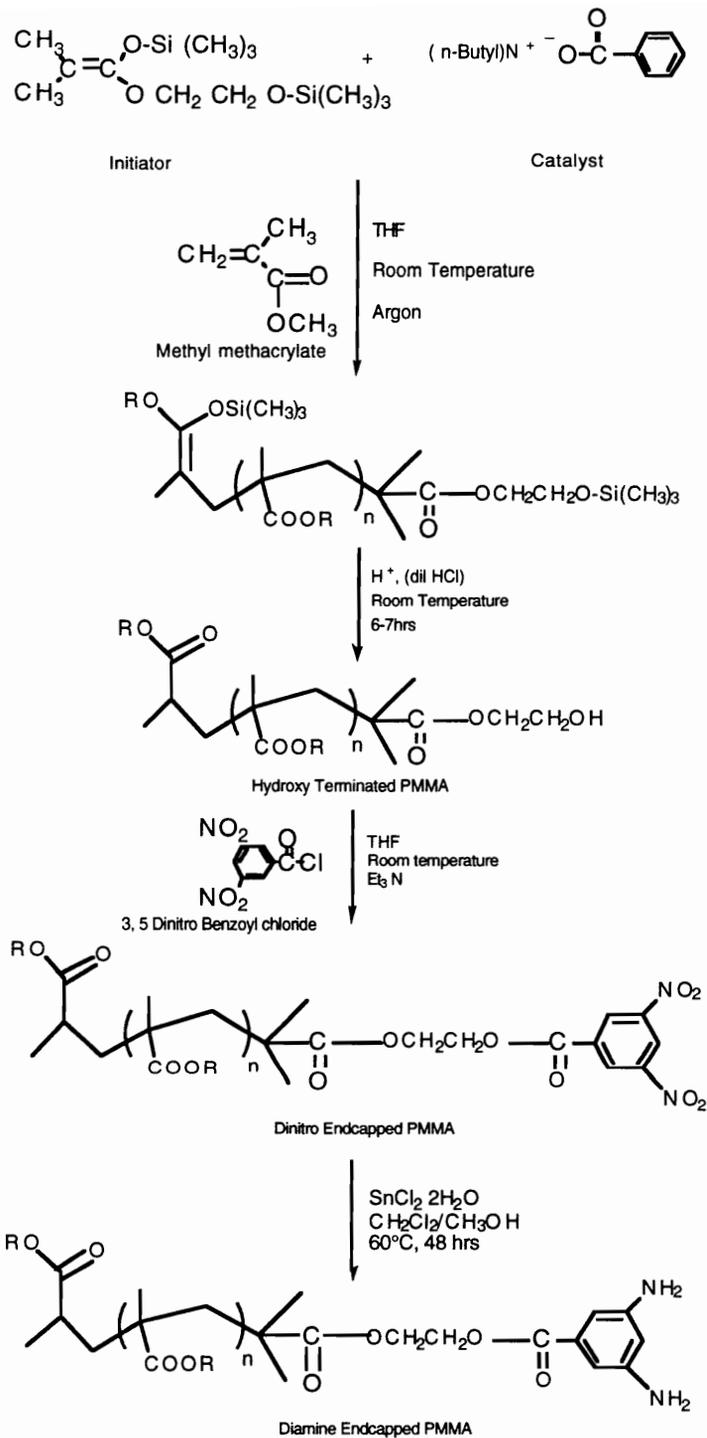


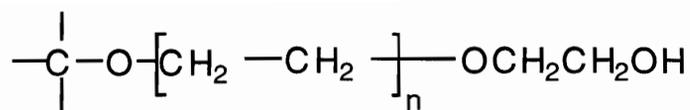
Figure 3.3.1.4 Synthesis of 3,5-diaminobenzoate terminated poly(methyl methacrylate) macromonomer

the combined filtrates concentrated on a rotovap and the resulting polymer solution was then precipitated into a rapidly stirred 10 fold volume excess of methanol. The polymer was filtered, washed with hexanes and dried in a vacuum oven at room temperature. The extent of end functionalization was monitored using ^1H NMR. The dinitro functionalized polymer was then redissolved in 75 mL of 2:1 methanol/methylene chloride mixture, 1.55 g of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (6.8 mmol) was added and the mixture was hydrogenated in a conventional glass apparatus for about 48 hours, maintaining the temperature at 65°C . The extent of hydrogenation was monitored using ^1H NMR. The hydrogenated mixture was filtered through a bed of celite and concentrated in a rotovap. The resulting solution was then precipitated into a rapidly stirred 10 fold volume excess of methanol. The polymer was filtered, washed with methanol followed by hexanes and dried in a vacuum oven at room temperature. This yielded the diamino-terminated PMMA oligomer as white solid. The extent of reduction was confirmed using a ^1H NMR and thorough potentiometric titration of the amine against HBr in acetic acid. The molecular weight of the oligomer was determined to be 7500 g/mole.

3.3.1.6 3,5-Diaminobenzoate terminated polyethylene oxide macromonomer

5000 g/mole mono hydroxy terminated PEO was obtained from Union Carbide Corporation. Prior to use, 50 g of the polymer was dissolved in hot THF and precipitated into a rapidly stirred 10 fold volume excess of hexanes to remove any impurities. The polymer was filtered dried and stored in a desiccator to prevent moisture uptake by the polymer. The general procedure for the functionalization of PEO oligomers with 3,5-diamino benzoate end group is given for 5000 g/mol oligomer as depicted in Figure 3.3.1.5. To a two necked, 100 mL, round bottom flask equipped with a stir bar, argon inlet and a condenser was added 15 g (3.0 mmol) of monofunctional hydroxy PEO oligomer of molecular weight 5000 g/mole. The polymer was heated to 60°C and dried

overnight in under high vacuum typically 50-200 mtorr. To this, 1.1g (0.015 moles) pyridine was added, followed by 150 mL of freshly distilled tetrahydrofuran (THF). The mixture was cooled in ice and to this 3.456 g (0.015 moles) 3,5-dinitro benzoyl chloride was added in one portion and the mixture stirred for 24 hours. The precipitated pyridinium hydrochloride salt was observed to form and then slowly was observed to dissolve back into the reaction mixture. After the reaction was complete, the solution was then filtered over celite, and the filtrates concentrated on a rotovap. The viscous solution was precipitated into a five fold by volume excess of rapidly stirring hexanes. The precipitated functionalized oligomer was filtered and immediately dissolved in hot acetone and cooled to below 0°C, which resulted in white crystals of PEO oligomer. Using this procedure it was easy to separate the pyridinium salts from the functionalized oligomer. The crystals were filtered and dried in a vacuum oven at room temperature. The oligomer was recrystallized thrice to obtain pure dinitro functionalized PEO oligomer. The extent of end functionalization of PEO oligomer was monitored using ^1H NMR. The dinitro functionalized PEO oligomer was then redissolved in 3:1 mixture of THF/ CH_2Cl_2 , 200 mg of $\text{Pd}(\text{OH})_2$ on activated carbon was added and the mixture was catalytically hydrogenated in a Parr hydrogenator apparatus for about 48 hours at 10 psi hydrogen pressures. The hydrogenated mixture was filtered through a bed of celite and activated charcoal and the THF solution concentrated. The resulting diamino derivative was azeotroped with toluene to facilitate drying. The excess toluene was then distilled from the flask and finally with a kugelrohr at 125°C (20 mm/Hg) to remove residual toluene. This yielded the diamino terminated PEO oligomer as a brown solid. The extent of reduction was confirmed using a ^1H NMR and thorough potentiometric titration of the amine against HBr in acetic acid. The number average molecular weight of the oligomer was determined to be 5300 g/mole.



Hydroxy Terminated PEO Oligomer

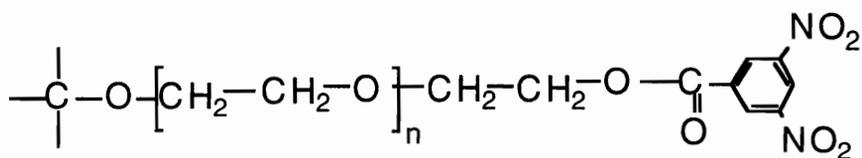
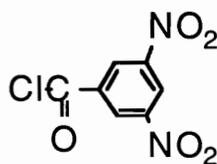
1) Reprecipitate from THF/ hexane mixture

2) Heat

3) Pull vacuum overnight

4) Dry THF

5) Pyridine



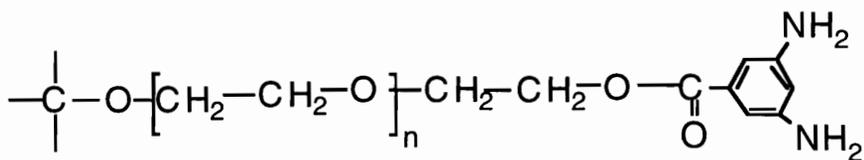
Dinitro Benzoate terminated PEO

1) Precipitated from hexane

2) Recrystallized from Acetone

3) Redissolved in CH₂Cl₂ / THF

4) Pd(OH)₂, H₂, Room temp



Diamino Benzoate Terminated PEO

Figure 3.3.1.5 Synthesis of 3,5-diaminobenzoate terminated PEO macromonomer

3.3.2 Synthesis of Polymers

High molecular weight polyimide homopolymer, poly(propylene oxide)-polyimide block copolymer, poly(propylene oxide)-polyimide graft copolymer, poly(ethylene oxide)-polyimide graft copolymer, poly(methyl methacrylate)-polyimide graft copolymer and polyimide oligomers studied in this research were synthesized by combining a diamine and a dianhydride or diacyl chloride diester of the appropriated dianhydride to form the polyimide precursor, the poly(amic acids) or the poly(amic alkyl ester)s. The poly(amic acids) was cyclodehydrated using chemical imidization technique in the presence of acetic anhydride and pyridine to afford the respective polyimide. The poly(amic alkyl ester)s were converted to the polyimide using thermal imidization technique. Ethynyl terminated poly(amic alkyl ester) oligomers were synthesized using 3-aminophenyl acetylene as the monofunctional reagent both to control the molecular weight and the endgroup.

All the polymers were synthesized in a thourree neck, round bottom flask equipped with an Ar gas inlet, an overhead mechanical stirrer and an additional funnel. The apparatus was flame dried prior to use with a Bunsen burner. An argon purge was maintained thorough the flask while drying and during the polymerization. Synthetic procedures will be outlined for the synthesis of high molecular weight polyimides, polyimide copolymers and polyimide oligomers.

Molecular weight control was achieved by adding a monofunctional endcapper to obtain functionalized polyimides by creating an stoichiometric imbalance in the functionalities. In order to synthesize both graft and block copolyimides containing the desired amount (wt.%) of the block or the graft in the polyimide matrix, relative amounts of the monomers needed for the polymerization had to be calculated. This was achieved by using the Carothers equation.²⁰² A sample calculation for the synthesis of a 5g batch of PMDA/3FDA polyimide - poly(propylene oxide) block and graft copolymer containing 25 wt.% of poly(propylene oxide) is provided in Figure 3.3.2.1.

$$\text{Grams of copolymer desired} = 5.0\text{g}$$

$$\begin{aligned} \text{wt.\% of the poly(propylene oxide) of molecular weight 4100 g/mole to be incorporated} \\ = 25 \end{aligned}$$

$$\text{wt. of poly(propylene oxide) to be incorporated in a 5g batch} = 1.25 \text{ g}$$

$$\begin{aligned} \text{moles of poly(propylene oxide) to be incorporated in a 5g batch} &= 1.25\text{g} / 4100 \text{ g/mole} \\ &= 0.3048 \text{ mmole} \end{aligned}$$

$$\begin{aligned} \text{moles of polyimide} &= (5.0 - 1.25) / \text{mol. wt. of repeat unit} \\ &= 3.75 / 542.47 \\ &= 6.9128 \text{ mmole} \end{aligned}$$

	Block copolymer	Graft copolymer
moles of dianhydride (N_a)	6.9128 mmole	6.9128 mmole
moles of diamine (N_b)	$N_a - 2N_c = 6.7604 \text{ mmole}$	$N_a - N_b' = 6.608 \text{ mmole}$
moles of diamine macromonomer (N_b')	-	0.3048 mmole
moles of monoamine ($2N_c$)	0.3048 mmole	-

Figure 3.3.2.1 Sample Calculation for the Synthesis of Polyimide Block and Graft Copolymer

3.3.2.1 High molecular weight polyimides:

The following is a representative high molecular weight polyimide homopolymer polymerization procedure. The polymer synthesized was PMDA-3FDA polyimide of uncontrolled molecular weight. The polyimides were prepared in a two-stage process, which included the poly(amic acid) formation followed by chemical imidization. Thus, into a 100 mL reaction flask fitted with a argon inlet and outlet and a mechanical stirrer, was charged 3FDA (1.4198 g, 4.1476 mmol) and dry NMP (20 mL) under a argon blanket. Stirring was begun and after all the diamine had dissolved, PMDA (0.9047 g, 4.1476 mmol) was added as a powder to the stirring solution of the diamine. Additional NMP (10 mL) was used to insure complete addition of the dianhydride. The viscosity of the solution was observed to build quickly and the temperature was maintained at room temperature overnight under an argon. The viscous poly(amic acid) solution was then imidized chemically with acetic anhydride (3 mL) / pyridine (3 mL) mixture at 80°C for about 6-8 hours under argon atmosphere. The light yellow fibrous polymer was then isolated from the reaction solution by precipitation into methanol and dried in a vacuum oven at room temperature for 24 hours.

3.3.2.2 t-Butyl endcapped PMDA/3FDA meta-poly(amic alkyl ester) (mol wt. = 15,000 g/mole)

The poly(amic alkyl ester) endcapped with t-butyl phthalimide groups were prepared by adding meta-diethyl ester diacyl chloride dissolved in tetrahydrofuran to a solution of the diamine and the endcapper (t-butyl phthalic anhydride) in N-methyl pyrrolidinone (NMP) at 0°C, followed by stirring for 12 hours at room temperature under argon atmosphere.

A detailed procedure illustrating the synthesis of poly(amic alkyl ester)s endcapped with t-butyl phthalimide groups with a number average molecular weight of 15,000g/mole is provided. A thouree-necked flask equipped with an overhead stirrer and powder funnel

was charged with t-butyl phthalic anhydride (0.1909 g, 0.9346 mmol), 3FDA (4.000 g, 11.68 mmol) and dry NMP (30 mL) under a argon blanket. The powder funnel was carefully rinsed with excess 15 mL of NMP. The solution was cooled to 0°C and dry pyridine (3.2 mL) was added to the solution. Stirring was begun and after all the diamine had dissolved, the powder funnel was replaced with a pressure equalizing addition funnel. Meta-diethyl ester diacyl chloride (3.8937 g, 11.21 mmol) dissolved in freshly distilled dry tetrahydrofuran was added into the addition funnel via a syringe and then added dropwise into the reaction flask over a period of 1 hour. The polymerization was allowed to proceed overnight and the polymer was isolated by precipitation in methanol/water mixture. The precipitate was rinsed with water followed by methanol and dried in a vacuum oven at room temperature for 48 hours. A similar procedure was used in the synthesis of the t-butyl endcapped PMDA/3FDA para poly(amic alkyl ester).

3.3.2.3 PMDA/3FDA polyimide-poly(propylene oxide) block copolymers.

Block copolymers were prepared in a two-stage process that included the poly(amic acid) formation followed by chemical imidization. Into a 100 mL reaction flask fitted with an argon inlet and an outlet and a mechanical stirrer, were charged monoamine terminated PO macromonomer (0.5g, 0.217 mmol), 3FDA (0.9359 g, 2.733 mmol) and dry NMP (20 mL) under a argon blanket. Stirring was begun and after all the diamine had dissolved, PMDA (0.62 g, 2.842 mmol) was added as a powder to the stirring solution of the diamine. Additional NMP (10 mL) was used to insure complete addition of the dianhydride to the reaction. The viscosity of the solution was observed to build quickly and the temperature was maintained at room temperature overnight under argon. The viscous poly(amic acid) solution was then imidized chemically with acetic anhydride (1.611 mL) / pyridine (1.38 mL) mixture at 80°C for about 6-8 hours under argon atmosphere. The polymer was then isolated from the reaction solution by precipitation into methanol and

then dried in a vacuum oven at room temperature for 24 hours. The dried polymer was stirred overnight in methanol to remove any unreacted PO macromonomers, filtered and dried in vacuum oven at 100°C for 24 hours.

3.3.2.4 Polyimide-poly(propylene oxide) graft copolymers.

A typical procedure for the synthesis of polyimide based graft copolymers is provided. Graft copolymers were prepared in a two-stage process that included the poly(amic acid) formation followed by chemical imidization. Into a 100 mL reaction flask fitted with a argon inlet, an outlet and a mechanical stirrer were charged diamine terminated PO macromonomer (750 mg, 0.2174 mol), 3FDA (1.3456 g, 3.9303 mmol) and dry NMP (20 mL) under an argon blanket. Stirring was begun and after all the diamine had dissolved, PMDA (0.9047 g, 4.1476 mmol) was added as a powder to the stirring solution of the diamine. Additional NMP (10 mL) was used to insure complete addition of the dianhydride to the reaction. The viscosity of the solution was observed to build quickly and the temperature was maintained at room temperature overnight under argon. The viscous poly(amic acid) solution was then imidized chemically with acetic anhydride (3 mL) / pyridine (3 mL) mixture at 80°C for about 6-8 hours under argon atmosphere. The polymer was then isolated from the reaction solution by precipitation into methanol and then dried in a vacuum oven at room temperature for 24 hours. The dried polymer was stirred overnight in methanol to remove any unreacted PO macromonomers, filtered and dried in vacuum oven at 100°C for 24 hours. Similar procedures were used to synthesize other graft copolymers such as poly(ethylene oxide)-polyimide graft copolymer, or poly(methyl methacrylate)-polyimide graft copolymer, by appropriately changing the amounts of the co-macromonomer, i.e., diamine terminated PEO and PMMA.

3.3.2.5 PMDA/3FDA meta-poly(amic alkyl ester)-poly(propylene oxide) graft copolymer

The poly(amic alkyl ester) poly(propylene oxide) graft copolymers were prepared by adding meta-diethyl ester diacyl chloride dissolved in tetrahydrofuran to a solution of the diamine and the diamine terminated poly(propylene oxide) coblock in N-methyl pyrrolidone (NMP)/pyridine mixture at 0°C, followed by stirring for 12 hours at room temperature under an argon atmosphere.

A detailed procedure illustrating the synthesis of poly(amic alkyl ester)s poly(propylene oxide) copolymer containing 25 wt.% of the poly(propylene oxide) coblock of number average molecular weight of 3100 g/mole is provided. A thourree-necked flask equipped with an overhead stirrer and powder funnel was charged with poly(propylene oxide) (0.750 g, 0.2174 mmol), 3FDA (1.3456 g, 3.9303 mmol) and dry NMP (15 mL) under a argon blanket. The powder funnel was carefully rinsed with an excess (15 mL) of NMP. The solution was cooled to 0°C and dry pyridine (0.7 mL) was added to the solution. Stirring was begun and after all the diamine had dissolved, the powder funnel was replaced with a pressure equalizing addition funnel. Meta-diethyl ester diacyl chloride (1.4399 g, 4.1477 mmol) dissolved in freshly distilled dry tetrahydrofuran was added into the addition funnel via a syringe and then added dropwise into the reaction flask over a period of 1 hour. The polymerization was allowed to proceed overnight and the polymer was isolated by precipitation in methanol/water mixture. The precipitate was rinsed with water followed by methanol and stirred overnight in methanol to remove unreacted poly(propylene oxide). The polymer was filtered and dried in a vacuum oven at room temperature for 24 hours at 60°C.

3.3.2.6 Ethynyl terminated PMDA/3FDA polyimide(M. wt = 3000g/mole).

The poly(amic acid) were prepared by adding the dianhydride to a solution of the diamine and the endcapper(3-ethynyl aniline) in N-methyl pyrrolidinone (NMP) followed by stirring for 12 hours at room temperature under an argon atmosphere. The poly(amic acid) were then chemically imidized to the respective polyimides using acetic anhydride and pyridine mixture at 70°C.

The following example illustrates the synthesis of polyimides with a number average molecular weight of 3000 g/mole, which were endcapped with ethynyl groups. Into a 100 mL reaction flask fitted with a argon inlet, an outlet and a mechanical stirrer, were charged 3-ethynyl aniline (0.431, 3.6868 mmol), 3FDA (3.155 g, 9.217 mmol) and dry NMP (30 mL) under a argon blanket. Stirring was begun and after all the diamine had dissolved, PMDA (2.4125 g, 11.1 mmol) was added as a powder to the stirring solution of the diamine. Additional NMP (10 mL) was used to ensure complete addition of the dianhydride to the reaction. The viscosity of the solution was observed to increase and the temperature was maintained at room temperature overnight (12 hours) under argon atmosphere. The poly(amic acid) solution was then imidized chemically with acetic anhydride (6.5 mL) / pyridine (5.5 mL) mixture at 70°C for about 6-8 hours under argon atmosphere. The polymer was later isolated by precipitation into methanol and dried in a vacuum oven at room temperature for 24 hours.

Using the above procedure, ethynyl terminated polyimides of theoretical number average molecular weights of 3000 g/mole, 6000 g/mole and 12000 g/mole were synthesized.

3.3.2.7 Ethynyl terminated PMDA/3FDA meta-poly(amic alkyl ester) oligomers (M. wt = 3000g/mole).

The poly(amic alkyl ester) endcapped with ethynyl groups were prepared by adding meta-diethyl ester diacyl chloride dissolved in tetrahydrofuran to a solution of the diamine and the endcapper (3-ethynyl aniline) in N-methyl pyrrolidinone (NMP) at 0°C, followed by stirring for 12 hours at room temperature under argon atmosphere.

A detailed procedure illustrating the synthesis of poly(amic alkyl ester)s endcapped with ethynyl groups with a number average molecular weight of 3000g/mole is provided. A threenecked flask equipped with an overhead stirrer and powder funnel was charged with 3-ethynyl aniline (0.7162, 6.1 mmol), 3FDA (5.2646 g, 15.4 mmol) and dry NMP (30 mL) under a argon blanket. The powder funnel was carefully rinsed with excess 15mL of NMP. The solution was cooled to 0°C and dry pyridine (2.93 g, 37 mmol) was added to the solution. Stirring was begun and after all the diamine had dissolved, and the powder funnel was replaced with a pressure equalizing addition funnel. Meta-diethyl ester diacyl chloride (6.399 g, 18.4 mmol) dissolved in freshly distilled dry tetrahydrofuran was introduced into the addition funnel with a syringe and then added dropwise into the reaction flask over a period of 1 hour. The polymerization was allowed to proceed overnight and the polymer was isolated by precipitation in methanol/water mixture. The precipitate was rinsed with water followed by methanol and dried in a vacuum oven.

Using the above procedure, ethynyl terminated poly(amic alkyl ester) of theoretical number average molecular weights of 3000 g/mole, 6000 g/mole and 12000 g/mole have been synthesized.

3.3.2.8 High molecular weight PMDA/3FDA meta-poly(amic alkyl ester) containing pendant ethynyl groups.

The poly(amic alkyl ester) containing pendant ethynyl groups were prepared by adding meta-diethyl ester diacyl chloride dissolved in tetrahydrofuran to a solution of the diamine(3FDA) containing different mole percent of diamine containing pendant ethynyl groups (EDA) in N-methyl pyrrolidinone (NMP) at 0°C, followed by stirring for 12 hours at room temperature under argon atmosphere.

A detailed procedure illustrating the synthesis of poly(amic alkyl ester)s with 40 mole percent pendant ethynyl groups is provided. A thourree-necked flask equipped with an overhead stirrer and powder funnel was charged with EDA (2.6937, 7.36 mmol), 3FDA (3.774 g, 11.04 mmol) and dry NMP (50 mL) under a argon blanket. The powder funnel was carefully rinsed with excess 15mL of NMP. The solution was cooled to -5°C and dry pyridine (2.926 g, 37 mmol) was added to the solution. Stirring was begun and after all the diamine had dissolved, and the powder funnel was replaced with a pressure equalizing addition funnel. Meta-diethyl ester diacyl chloride (6.399 g, 18.4 mmol) dissolved in freshly distilled dry tetrahydrofuran was added to introduced into the addition funnel with a syringe and the addition funnel was adjusted for dropwise addition of the diethyl ester diacyl chloride solution into the reaction flask over a period of 1 hour. The polymerization was allowed to proceed overnight and the polymer was isolated by precipitation in methanol/water mixture. The precipitate was rinsed with water followed by methanol and dried in a vacuum oven.

Using the above procedure pendant ethynyl containing poly(amic alkyl ester) with 10, 20 and 40 theoretical mole percent of ethynyl groups along the chain have been synthesized.

3.3.2.9 Synthesis of ethynyl terminated PMDA/3FDA/poly(propylene oxide) meta-poly(amic alkyl ester) graft copolymer (M. wt = 3000 g/mole)

The PMDA/3FDA/poly(propylene oxide) graft copoly(amic alkyl ester) endcapped with ethynyl groups were prepared by adding meta-diethyl ester diacyl chloride dissolved in tetrahydrofuran to a solution of the diamines and the endcapper (3-ethynyl aniline) in N-methyl pyrrolidinone (NMP) at 0°C, followed by stirring for 12 hours at room temperature under argon atmosphere.

A thourree-necked flask equipped with an overhead stirrer and powder funnel was charged with 3-ethynyl aniline (0.2865 g, 2.445 mmol), 3FDA (2.0223 g, 5.906 mmol), diamine terminated PO macromonomer (1.0 g, 0.2439 mmol) and dry NMP (15 mL) under an argon blanket. The powder funnel was carefully rinsed with excess 15 mL of NMP. The solution was cooled to 0°C and dry pyridine (1.16 g, 17.74 mmol) was added to the solution. Stirring was begun and after all the diamine had dissolved, and the powder funnel was replaced with a pressure equalizing addition funnel. Meta-diethyl ester diacyl chloride (2.5598 g, 7.3736 mmol) dissolved in freshly distilled dry tetrahydrofuran was introduced into the addition funnel via a syringe and then added dropwise into the reaction flask over a period of 1 hour. The polymerization was allowed to proceed overnight and the polymer was isolated by precipitation in methanol/water mixture. The precipitate was rinsed with water followed by methanol. The polymer was stirred in methanol for 12 hours to remove any unreacted poly(propylene oxide), filtered and dried in a vacuum oven.

Using the above procedure ethynyl terminated poly(propylene oxide) grafted copoly(amic alkyl ester) of theoretical number average molecular weights of 3000 g/mole, containing 15, 25 and 40 wt% of the propylene oxide have been synthesized.

3.3.2.10 Synthesis of PMDA/3FDA/poly(propylene oxide) meta-poly(amic alkyl ester) block copolymer containing pendant ethynyl groups

A detailed procedure illustrating the synthesis of PMDA/3FDA/poly(propylene oxide) meta-copoly(amic alkyl ester)s containing 25 wt% of the poly(propylene oxide) and 40 mole percent pendant ethynyl groups is provided. A three-necked flask equipped with an overhead stirrer and powder funnel was charged with EDA (0.9674 g, 2.6431 mmol), 3FDA (1.3572 g, 3.964 mmol), diamine terminated PO macromonomer (1.25 g, 0.30487 mmol) and dry NMP (15 mL) under a argon blanket. The powder funnel was carefully rinsed with excess 15 mL of NMP. The solution was cooled to -5°C and dry pyridine (1.1 g, 13.90 mmol) was added to the solution. Stirring was begun and after all the diamine had dissolved, the powder funnel was replaced with a pressure equalizing addition funnel. Meta-diethyl ester diacyl chloride (2.3997 g, 6.912 mmol) dissolved in freshly distilled dry tetrahydrofuran was introduced into the addition funnel via a syringe, and the addition funnel was adjusted for dropwise addition of the diethyl ester diacyl chloride solution into the reaction flask over a period of 1/2 hour. The polymerization was allowed to proceed overnight and the polymer was isolated by precipitation in methanol/water mixture. The precipitate was rinsed with water followed by methanol and stirred in methanol for 12 hours to remove any unreacted poly(propylene oxide). The polymer was filtered and dried in a vacuum oven for 24 hours at room temperature.

3.4 CHARACTERIZATION OF POLYMERS AND MONOMERS

3.4.1 Titration of functional macromonomers

Titration techniques were employed in order to determine the molecular weight of the amine functionalized macromonomers used in the synthesis of both block and graft copolymers. An MCI GT-05 Automatic Titrator (Cosa Instruments Corp.) in conjunction with a standard glass-body combination electrode with Ag/AgCl reference electrode, was

used. The macromonomers to be titrated were dissolved in 1:1 chloroform / acetic acid mixture and titrated against approximately 0.025 N acetic acid solution of HBr. HBr solution was standardized by titrating against a standard solution of potassium hydrogen phthalate in acetic acid of known concentration. The procedure involved titrating a solution of a known weight (w) of the macromonomer in acetic acid /chloroform mixture against HBr of known normality (N). The ' M_n ' was estimated using the formula ($M_n = (2000 * w) / N * (B-B_1)$) where 'B' represents the volume of HBr used up by the polymer solution and 'B1' represents the blank titration value. If 'Pi' and 'Pe' represent the initial and endpoint 'milli-volt' potentials of the actual titration profile, then the blank titration value was estimated as the amount of titrant used up by acetic acid alone between the potential change (Pe-Pi). $\langle M_n \rangle$ was estimated as an average of 2 different titrations for each macromonomer.

3.4.2 Nuclear Magnetic Resonance Spectroscopy (NMR)

Proton NMR (^1H NMR) and Carbon 13 NMR (^{13}C NMR) spectra were taken on a Varian 400 MHz instrument in CDCl_3 or deuterated DMSO. All spectra were referenced to tetramethylsilane (TMS) at 0 ppm. This method was also used not only to calculate the number average molecular weight $\langle M_n \rangle$ of t-butyl phthalic acid end capped poly(amic alkyl ester)s and 3-aminophenyl acetylene endcapped polyimides and poly(amic alkyl ester)s, but also to assess the composition of the macromonomer in the copolymer by comparison of the integrating aromatic protons of the polyimide to that of the aliphatic protons of the macromonomer. In the case of the t-butyl phthalic acid end capped poly(amic alkyl ester)s, t-butyl protons were ratioed relative to the aromatic protons of the main chain to provide an estimate of $\langle M_n \rangle$ and for the 3-aminophenyl acetylene endcapped polyimides and poly(amic alkyl ester)s, the ethynyl carbons were ratioed against the aromatic carbons from the polymer backbone to estimate the $\langle M_n \rangle$. However, it should be

mentioned that the $\langle M_n \rangle$ obtained by this method was based on the assumption that there are two targeted endgroups per chain.

3.4.3 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR was used to obtain IR spectra of the final polymers and monomers using a Nicolet MX-1 spectrophotometer. Polymer samples were analyzed by casting thin films on salt plates and monomers were run as KBr pellets. FTIR was used to measure the extent of imidization of polymer samples by examining the spectral imide bands at 1778 cm^{-1} , 1728 cm^{-1} and 725 cm^{-1} .

3.4.4 Intrinsic and Inherent viscosity's

Intrinsic viscosity's were determined for all of the polyimide and poly(amic alkyl ester) homopolymers. Cannon-Ubbelohde dilution viscometer with various capillary sizes were used to collect data to determine intrinsic viscosity's. The polyimide and poly(amic alkyl ester) homopolymers were generally run in NMP at 25°C . The intrinsic viscosity values were obtained by using four different polymer concentrations and the results were linearly extrapolated to zero concentration. Inherent viscosity's were determined at a concentration of 0.5 g/dl .

3.4.5 Differential Scanning Calorimetry (DSC)

DSC was used to follow the imidization reaction of the alkyl ester groups to the imide group in poly(amic alkyl ester), the crosslinking reaction of the ethynyl groups in the ethynyl terminated poly(amic alkyl ester) homopolymers and also to obtain the lower glass transition temperatures of the polyimide copolymers. DSC was conducted on a Perkin Elmer Model DSC 7. DSC scans were run under nitrogen atmosphere at 10°C per minute.

The T_g values were obtained from a second heating cycle after rapid cooling from above the T_g of the polymer samples.

3.4.6 Thermogravimetric Analysis (TGA)

Dynamic TGA was performed on a Perkin Elmer TGA 7 in order to determine the relative stability's of the polyimide homopolymers and polyimide block and graft copolymers. The composition of the propylene oxide in the copolymer was also assessed using TGA, by measuring the weight retention after decomposition of the thermally labile block. Thin films were placed in a platinum pan. The samples were heated at a rate of 10°C per minute in an air atmosphere. Weight loss of the samples was measured as a function of time and temperature. The thermal stability of the polymers is generally reported as the temperature for 5 wt.% loss. Isothermal TGA were also run on the same instrument under both air and nitrogen atmosphere. The samples were held at a constant temperature and the weight loss was measured as a function of time. Isothermal TGA was used to establish the processing window for film and foam formation of 3FDA / PMDA copolymers.

3.4.7 Thermo Mechanical Analysis (TMA)

In order to determine the coefficient of thermal expansion of the polyimide films, thermomechanical analysis was performed on the films using a Perkin Elmer TMA 7 series thermo mechanical analyzer. The measurements were carried out during expansion with a heating rate of $5^\circ\text{C} / \text{min}$. in a nitrogen atmosphere at a load of 1 g. The CTE values were obtained as a mean over the range of $50 - 250^\circ\text{C}$.

3.4.8. Dynamic Mechanical Analysis (DMA)

In order to determine the glass transition temperature of the polyimide homopolymer, and that of the copolymers, dynamic mechanical analysis (DMA) was performed. DMA was carried out on polymer films using a Seiko Model 200 DMS or a Perkin-Elmer DMA-7. The storage modulus, loss modulus and tan delta were obtained for all samples run. Tests were conducted at a frequency of 1Hz employing a dynamic temperature scan rate of 2°C/min. DMA was also used to monitor the efficiency of crosslinking reaction in the case of the ethynyl terminated materials.

3.4.9. Dynamic Mechanical Thermal Analysis (DMTA)

DMTA was also used to determine the glass transition temperature of the polyimide homopolymers and that of some copolymers. DMTA was carried out on polymer films using a Polymer Laboratories DMTA analyzer. The storage modulus, loss modulus and tan delta were obtained for all samples run. Tests were conducted at a frequency of 1Hz, employing a dynamic temperature scan rate of 10°C/min.

3.4.10 Density Measurements

Density measurements were used as a tool to monitor the efficiency of the foam process. Density measurements were obtained with a density gradient column made from water and a concentrated solution of calcium nitrate. The column was standardized using calibrated density beads whose density ranged from 1.05 g/cm³ to 1.45 g/cm³. These measurements were carried out on polymer films. The density values were obtained by using two different polymer samples and the results were averaged.

3.4.11 Small Angle X-ray Scattering Measurements (SAXS)

Small angle X-ray scattering (SAXS) was carried out using a Siemen's Kratky camera system in conjunction with a M. Braun position sensitive detector system from Innovative Technology. The generator used was a Philips table top generator PW 1729 operating at 40KV and 20mA. CuK α radiation having a wavelength of 1.54 \AA was used. A nickel filter was used to remove low energy radiation. SAXS measurements were performed on both the foamed and the unfoamed polyimide films to monitor the efficiency of the foaming process.

3.4.12 Transmission Electron Microscopy (TEM)

Transmission Electron Microscopy was performed on a Phillips I2 520 instrument at 100kV. Polyimide block and graft copolymer films were cast from a dilute solution of the copolymer in NMP onto a glass plate and complete removal of the solvent was accomplished by heating the polymer films to 300 $^{\circ}\text{C}$ at 5 $^{\circ}\text{C}/\text{min}$. and maintaining at 300 $^{\circ}\text{C}$ for 1 hour in a nitrogen atmosphere. Films were prepared for each sample by mounting in an epoxy matrix and ultra microtoming them at room temperature to study the morphology of the foam.

3.4.13 Refractive Index Measurements

Refractive Index Measurements were performed on a Metricon-PC 2000 instrument connected to a photo detector using a helium-neon laser of wavelength 642.8 nm. These measurements were performed on a 2-3 microns thick films prepared by spin coating onto a 1" quartz wafer. The refractive index values were obtained by using thourree different polymer samples and the results were averaged. The measure of the refractive index provides an insight to the approximate dielectric constant of the material. The dielectric

constant " ϵ " of a nonpolar insulator may be expressed in terms of the refractive index " n " by Maxwell's relationship: $\epsilon = n^2$.

3.4.14 Thin Film Stress Measurements

Preliminary thin film stress measurements were performed on a Flexus thin film stress measuring apparatus using a laser of wavelength 632 nm with a spot diameter of 1 mm. The films were spin coated onto 4" diameter silicon wafers and ranged in thickness from 5 - 9 microns. In all cases, Union Carbide A-1100 (3-aminopropyl triethoxy silane) diluted to 0.2 weight percent in 95:5 methanol : water mixture was used as the adhesion promoter. TFS as a function of temperature was performed on substrate at 10°C / min. up to 400°C on both the homopolymer and foamed polymer

3.4.15 Solubility Parameter Determination

The solvents used in the solubility parameter study were methyl isobutyl ketone($d_1 = 8.4$), chloroform($d_1 = 9.3$), tetrahydrofuran($d_1 = 9.1$), acetone($d_1 = 9.9$), pyridine($d_1 = 10.7$), nitrobenzene($d_1 = 10$), dimethylacetamide($d_1 = 10.8$), n-methylpyrrolidone($d_1 = 11.2$), dimethylformamide($d_1 = 12.1$), dimethylsulfoxide($d_1 = 12$), methanol ($d_1 = 14.5$), glycerol($d_1 = 16.5$), and water($d_1 = 23.4$). Solubility parameters in $(\text{cal/cc})^{1/2}$ of the above solvents were obtained from reference.²⁰³ Solvent uptake studies were performed on a cured 3000 g/mol ethynyl endcapped polyimide. Samples in the form of films were all of approximately constant geometry and cured using the same cure cycle. Cured samples were kept immersed in various solvents at 25°C in tightly sealed sample vials. The gain in weight, if any, of the samples was monitored over a period of 48 to 72 hours.

3.3.4.16 Electron Spin Resonance Spectroscopy

Electron paramagnetic resonance was performed on an IBM ER 200 D-SRC instrument operating at 9.55 GHz.

3.5 FOAM FORMATION

Polyimide-poly(propylene oxide) (PI-PO) block and graft copolymer films were cast from a dilute solution (10%) of the copolymer in NMP onto a glass plate and complete removal of the solvent was accomplished by heating the polymer films to 300°C at 5°C/min. and maintaining this temperature for 1 hour in a nitrogen atmosphere. The films were then cooled to room temperature and reheated at a rate of 5°C/min. to 270°C, in the case of the copolymer having PO labile block of molecular weight of 3450 g/mole. The temperature was raised to 300°C, in the case of copolymers having a PO labile block of molecular weight 8000 g/mole, and was maintained at the respective temperatures of 270 or 300°C for 10 hours in air. Similar procedures were used in the case of polyimide -poly(methyl methacrylate) copolymers and also in the case of polyimide - poly(ethylene oxide) copolymers. In the case of the crosslinked foams, the materials were first cast from a dilute solution of the copolymer in NMP onto a glass plate. Crosslinking and complete removal of the solvent was accomplished by heating the polymer films to 300°C at 25°C/min. and maintaining the films at 300°C for 3 hour in a nitrogen atmosphere. The films were then cooled to room temperature and subsequently foamed in air at 270°C for 8 to 10 hours.

4.0 - RESULTS AND DISCUSSION

4.1 INTRODUCTION

The results and discussion have been subdivided into several sections. Because all the work presented in this investigation relates to the polyimide structure derived from pyromellitic dianhydride (PMDA) and 1,1-bis(4-aminophenyl)-1-phenyl-2,2,2-trifluoroethane (3FDA), the first section deals with the synthesis and characterization of the homopolyimide derived from PMDA and 3FDA. The approach used to generate a polyimide foam in this investigation was to cast well defined microphase separated copolymers based on a thermally stable polyimide block and thermally labile block. Upon thermal treatment, the thermally unstable block was expected to undergo thermolysis generating micropores closely related in size to that of the precursor block and graft copolymers.

Design of a multi-phase polyimide copolymer comprising a thermally unstable component can be approached in two ways, either via the synthesis of a block or graft copolymer. Thus, the second section deals with the synthesis of PMDA/3FDA based polyimide-poly(propylene oxide) ABA-type block copolymers. The synthesis, characterization, and drawbacks of micro or “Nano” foams obtained from block copolymers are also included in this section. This led us to investigate the graft copolymer approach, where the thermally labile grafts are attached to a polyimide backbone. Thus, the third section deals with synthesis, characterization and some problems associated with this approach. Section Four deals with the synthesis and characterization of polyimide foams developed from poly(propylene oxide)-poly(amic alkyl ester) graft copolymers. This approach was undertaken in an attempt to develop good thin film coatings of the graft

copolymers. In order to develop polyimide foams that are resistant to solvents, thermosetting polyimide foams were investigated and this is discussed in Section Five.

Investigation of other polymers, in addition to poly(propylene oxide), as the labile group includes poly(ethylene oxide) and poly(methyl methacrylate) graft copolymers. The two systems led to some very interesting and unexpected results. These results and our attempts to generate foams from them are discussed in Sections 6 and 7, respectively.

4.2 HIGH T_g PROCESSIBLE HOMOPOLYIMIDE

4.2.1 Synthesis and properties of PMDA-3FDA polyimide

PMDA-3FDA polyimide synthesis is depicted in Figure 4.2.1.1. This polyimide was first reported by McGrath et al.¹⁹⁹ It was prepared using the conventional two-step polyimide synthesis procedure, where solution imidization was demonstrated to be a crucial step. The first step, is the formation of the poly(amic acid), was accomplished by dissolving the diamine 3FDA in a polar aprotic solvent, NMP. To this, dianhydride was added as a solid and rinsed in with NMP, bringing the final concentration to 25 weight % solids. The solution was stirred at ambient temperature until it became homogeneous. The viscosity of the polymer solution was observed to increase immediately, indicating the formation of the poly(amic acid). The reaction was allowed to proceed for about 12 hours, which resulted in the formation of very highly viscous yellow poly(amic acid) solution.

In this thesis, cyclization of the poly(amic acid) to polyimide was accomplished via chemical imidization. Chemical imidization was achieved with excess acetic anhydride and pyridine for 6 - 8 hours at 80°C. At the end of the reaction, the solution was cooled, and the polymer was isolated by pouring the reaction mixture into methanol (10 parts of methanol for every one part of the polymer solution), which was rapidly stirred in a blender. The precipitated polyimide was collected by filtration and dried in a vacuum oven

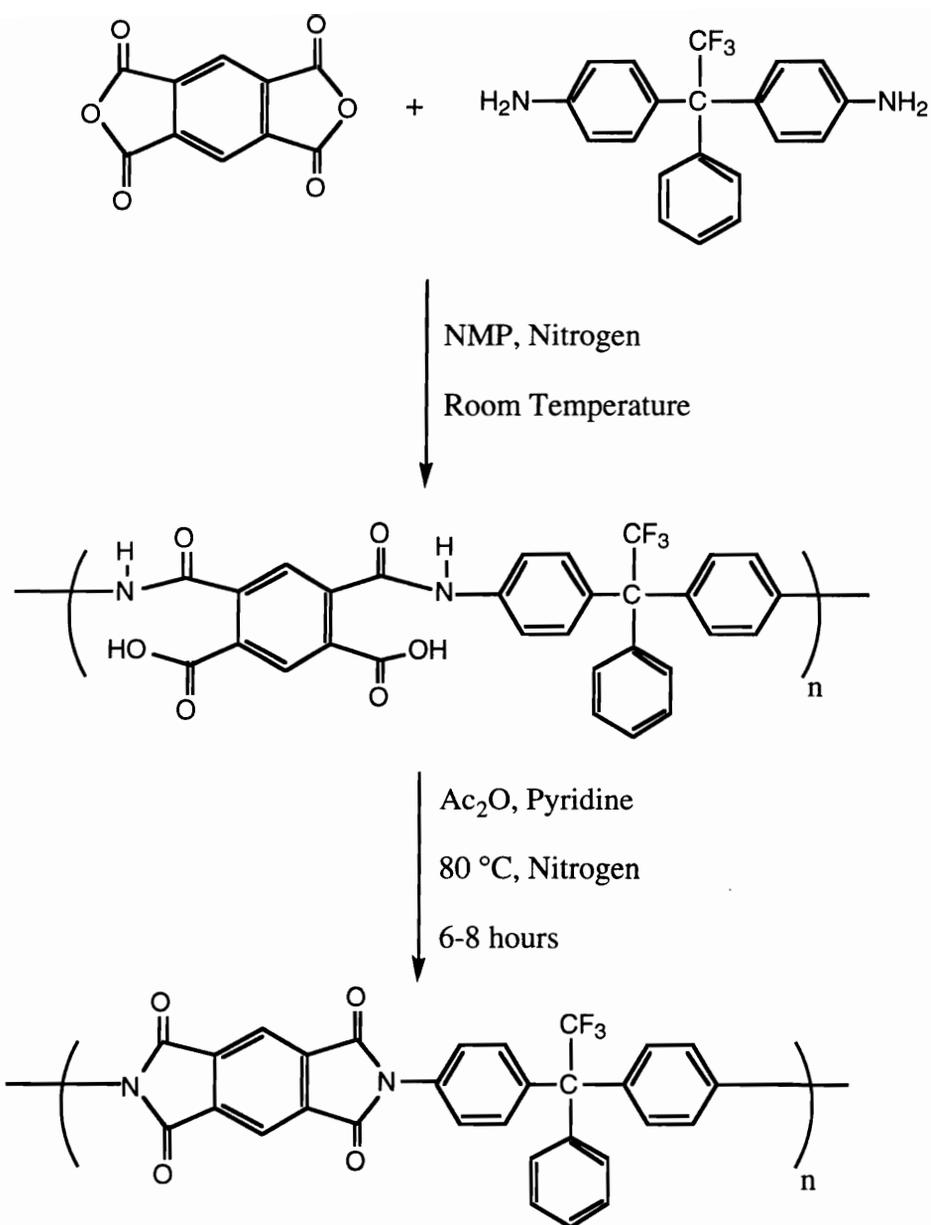


Figure 4.2.1.1 Synthesis of High Molecular Weight PMDA/3FDA Polyimide

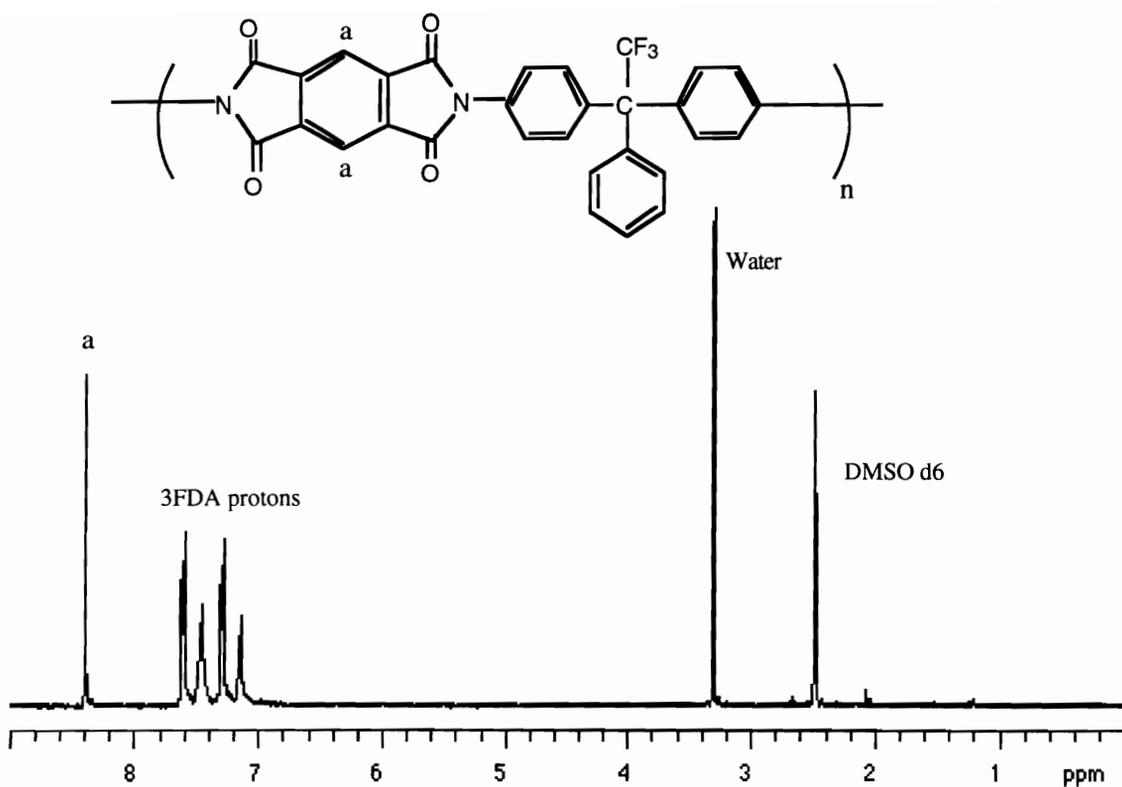


Figure 4.2.1.2 ^1H NMR of High Molecular Weight PMDA/3FDA Polyimide

at 200°C for 24 hours. No attempt was made to control the molecular weight` of the polyimide. The ¹H NMR spectrum of the homopolymer is provided in Figure 4.2.1.2.

The FTIR spectrum of the PMDA-3FDA polyimide is shown in Figure 4.2.1.3. The appearance of the characteristic imide infrared absorption peak band at 1775-1785 cm⁻¹ (asymmetric imide stretch) and 1710-1735 cm⁻¹(symmetrical imide stretch), followed by the disappearance of the amic acid absorption band at 1535 cm⁻¹, confirms that the polyimide is completely cyclized and the imidization is complete.

Intrinsic viscosity of the homopolymer was obtained in NMP at 25°C. The intrinsic viscosity was relatively high 0.75 dl/g, indicating that the molecular weight of the polyimide was greater than 30,000 g/mole, based on the earlier work done by Rogers et al.²⁰⁴

PMDA/3FDA polyimide was observed to be soluble in a wide range of polar aprotic solvents, such as NMP, DMSO, DMF, and DMAc. PMDA/3FDA polyimide was also found to be soluble in cyclopentanone. Poor solubility was observed in chlorinated and ether solvents, such as methylene chloride, chloroform, THF and diglyme. It is worth noting that the PMDA/3FDA polyimide is one of the few very high T_g polyimides that is soluble in its completely imidized form. This may be attributed to the presence of the bulky 1-phenyl-2,2,2-trifluoroethane linkage providing enough of a kink in the polymer chain to promote enhanced solubility of the polymer.

High molecular weight PMDA/3FDA polyimide was observed to have a glass transition temperature greater than 440°C, as measured from the maximum of the tan δ peak using dynamic mechanical analysis. A plot of the storage modulus(Pa) and Tan δ as a function of temperature(°C) is provided in Figure 4.2.1.4. The storage modulus was observed to undergo a sharp decline at around 450°C. The very high T_g of this polyimide could arise from the same bulky 1-phenyl-2,2,2-trifluoroethane linkage limiting the rotational conformations of the polymer chain.

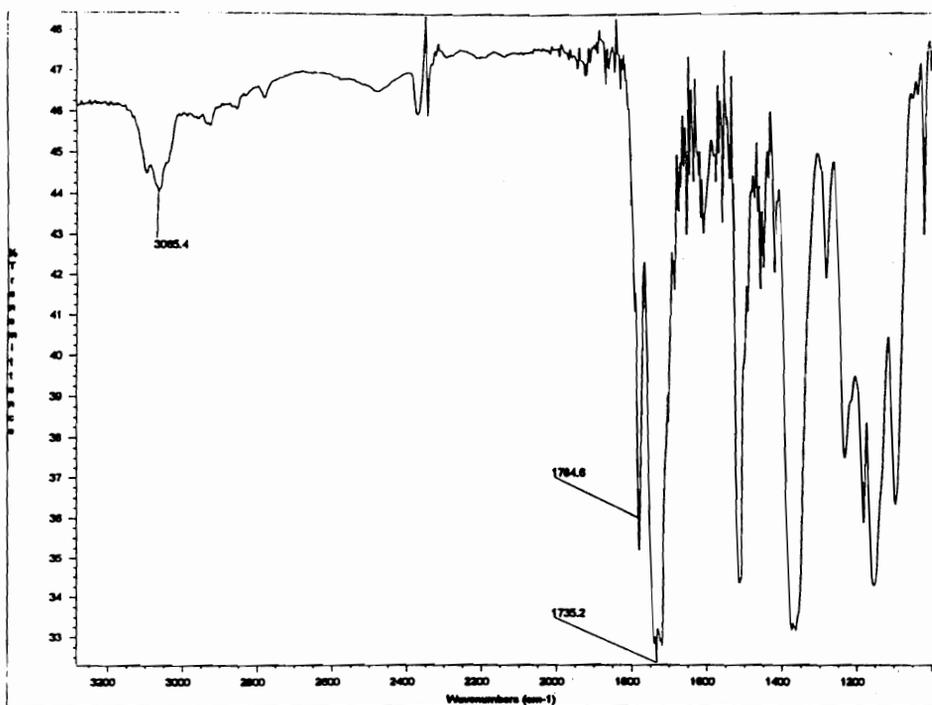
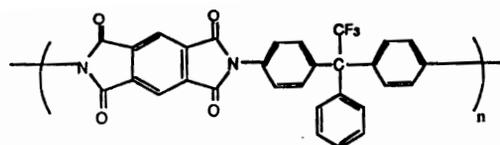


Figure 4.2.1.3 FTIR Spectrum of High Molecular Weight PMDA/3FDA Polyimide

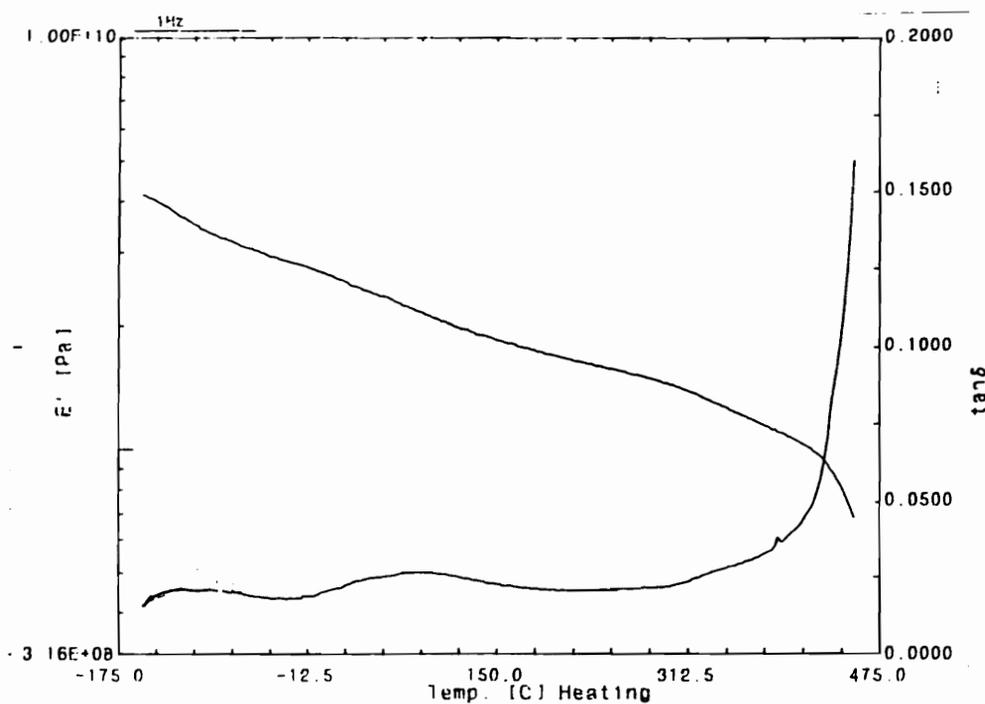
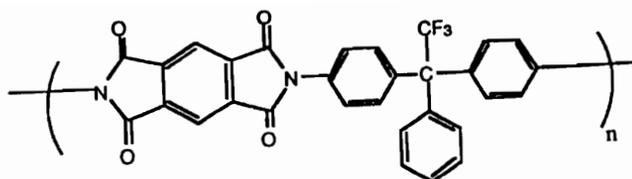


Figure 4.2.1.4 Dynamic Mechanical Analysis of High Molecular Weight PMDA/3FDA Polyimide (Heating Rate = 2°C/min, Frequency - 1Hz)

Dynamic thermogravimetric analysis (TGA) of the high molecular weight PMDA/3FDA polyimide demonstrated thermal stability above 525°C in air and above 550°C under nitrogen atmosphere. The 5% weight loss values were observed to be in the range of 570 to 580°C under nitrogen atmosphere. A typical dynamic TGA thermogram of PMDA/3FDA polyimide is provided in Figure 4.2.1.5. Isothermal TGA indicated very little weight loss occurring after 24 hours at 371°C in air and nitrogen.

The coefficient of thermal expansion of the PMDA/3FDA polyimide was also measured using Perkin Elmer TMA 7 thermo mechanical analyzer. In these experiments, a small tensile deformation was placed on the sample and heated. The deformation or displacement is plotted as a function of temperature and the derivative of this plot yielding the coefficient of thermal expansion. This is provided in Figure 4.2.1.6. The coefficient of thermal expansion was observed to be 67 ppm/°C, which is higher than the standard PMDA/ODA polyimide having a coefficient of thermal expansion of 31 ppm/°C.¹⁷⁹ It is important to note that in the TMA experiment, the sample expanded as expected up to 400°C. However, as the temperature approached the T_g or softening point, where an increase in the expansion rate was expected, the sample contracted substantially between 400 and 450°C. This unexpected contraction could presumably result from the residual stress arising from solvent evaporation as the film was made. The in plane stress of the fully cyclized PMDA/3FDA polyimide film was measured at 47.1 ± 2 MPa.

The refractive index of the high molecular weight PMDA/3FDA polyimide was also measured. The in plane refractive index of the polyimide film at 632.8 nm was found to be 1.62, and the out-of-plane refractive index was found to be 1.60, with a total difference of 0.02. The in plane and out-of-plane refractive index suggests the material is isotropic in nature. Thus, the PMDA/3FDA polyimide can be classified as a high T_g , amorphous, isotropic polyimide. The measure of the refractive index provides an insight into the approximate dielectric constant of the material. The dielectric constant calculated from the

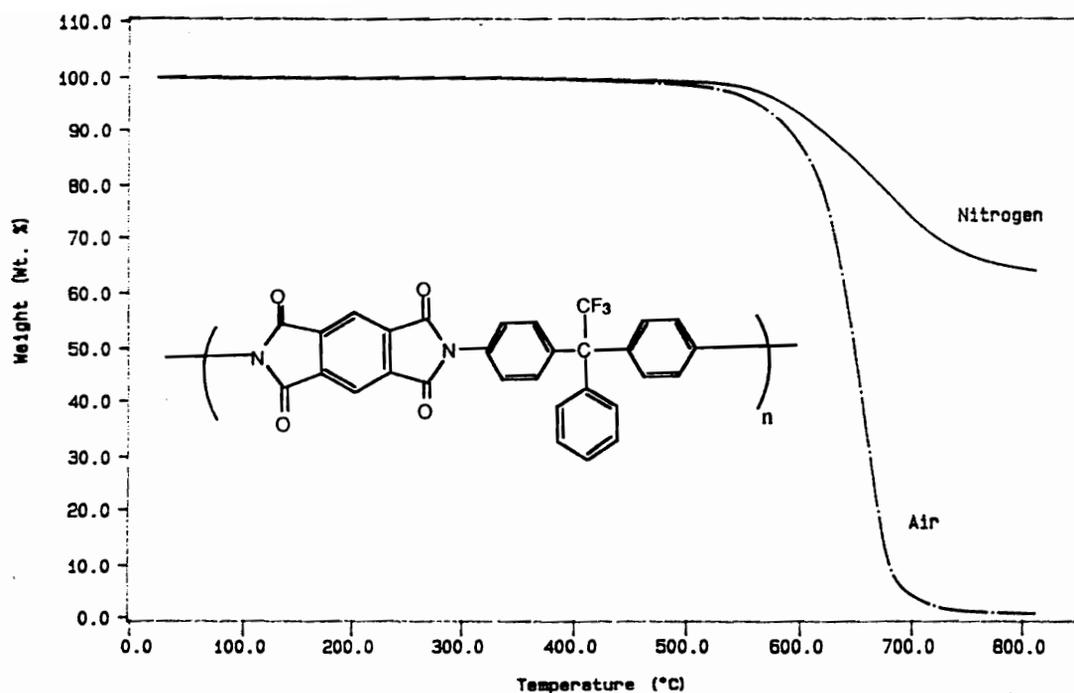


Figure 4.2.1.5 Dynamic TGA Thermogram of High Molecular Weight PMDA/3FDA Polyimide (Heating Rate 10°C/min)

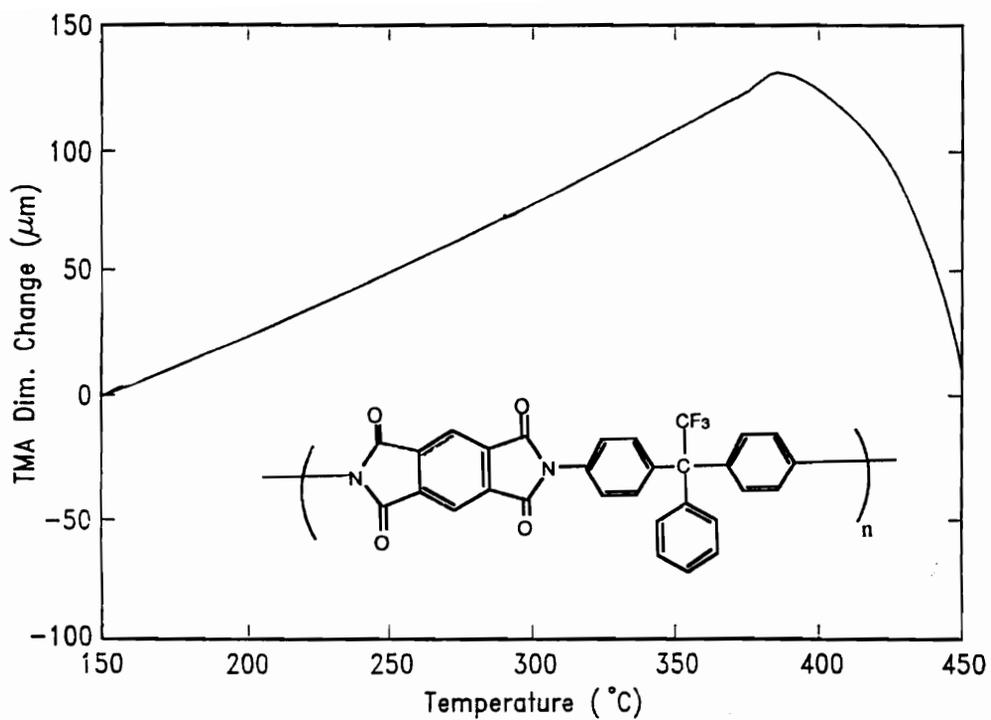


Figure 4.2.1.6 Displacement as a Function of Temperature, for a High Molecular Weight PMDA/3FDA Polyimide (Heating Rate 10°C/min)

refractive index using the Maxwell's relationship: $\epsilon = n^2$ was found to range from 2.56 to 2.62. These approximations due to the fact that ϵ is generally measured at relatively low frequencies ($10^2 - 10^6$ cycles / second), while as n is measured in the range of visible light (5 to 7 times 10^{14} cycles per second).

4.3 SYNTHESIS AND CHARACTERIZATION OF PMDA-3FDA BASED POLYIMIDE COPOLYMERS

4.3.1 Synthesis and characterization of polyimide foams from PMDA/3FDA based polyimide-poly(propylene oxide) ABA type block copolymers

The polyimide derived from 1,1-bis(4-aminophenyl)-1phenyl-2,2,2-trifluoroethane(3FDA) and pyromellitic dianhydride(PMDA) is one of the few high T_g (^a 450°C) polyimides that is amorphous, isotropic and soluble in organic solvents in the completely imidized form. Consequently, significant synthetic latitude is available, since the polymer and subsequent copolymers may be prepared through the poly(amic acid) or poly(amic alkyl ester) precursors, followed by the thermal cyclodehydration to the polyimide, or directly to the polyimide from the poly(amic acid) by chemical or solution imidization. This allowed us to prepare several triblock copolymers of PMDA/3FDA polyimide and monoamine terminated propylene oxide(PO) oligomer.

Block copolymers of PMDA / 3FDA and poly(propylene oxide) were prepared by a two-stage process, which included poly(amic acid) formation followed by imidization. Furthermore, the solubility of the resulting polyimide allowed the copolymer to be characterized under the different processing and foaming conditions surveyed.

The criteria for the thermally decomposable coblocks include the synthesis of well-defined functional oligomers, amenable towards copolymerization with polyimides, and subsequent quantitative decomposition of the labile block into non-reactive species that can readily diffuse through the glassy polyimide matrix. The decomposition temperature of the labile block has to be sufficiently high to permit standard film preparation and solvent removal procedures used by the microelectronics industry, but yet be well below the T_g of the polyimide block to avoid any possible collapse of the foam. Thus, the temperature

difference between the decomposition temperature of the labile block and the T_g of the high temperature polymer matrix defines the "processing window". The thermally decomposable coblock used in this study was poly(propylene oxide), as it decomposes well below the T_g of the homopolyimide derived from PMDA/3FDA. In fact, significant latitude is afforded by the use of poly(propylene oxide) as the labile component, since it is stable at temperatures as high as 300°C in an inert atmosphere, allowing solvent removal and imidization, if necessary. However, when exposed to oxygen, the decomposition temperature drops dramatically ($\approx 200^\circ\text{C}$) such that temperatures well below the T_g of many polyimides can be used to facilitate the foaming process. This is clearly shown in the dynamic TGA thermogram of an amine terminated poly(propylene oxide) of molecular weight 5000 g/mole, depicted in Figure 4.3.1.1 Thus, by employing a PMDA/3FDA based polyimide, a processing window of $\approx 200^\circ\text{C}$ is provided by using poly(propylene oxide) as the labile block. This variable decomposition temperature allows for a greatly enhanced processing window for fabrication of the film and subsequent foaming process.

Having determined the labile block to be used in the synthesis of the polyimide copolymer, the next step was to synthesize amine functionalized poly(propylene oxide) macromonomers to make the labile block amenable towards polyimide copolymerization. Thus, in order to synthesize polyimide-poly(propylene oxide) ABA type block copolymers, where A comprises the poly(propylene oxide) block and B comprises the polyimide block, monoamine functionalized poly(propylene oxide) macromonomers had to be synthesized. The approach taken to synthesize the monoamine terminated poly(propylene oxide) macromonomers was to first synthesize monohydroxy terminated poly(propylene oxide), transform the hydroxyl end group of the propylene oxide oligomer to aromatic

monofunctional nitro group, and reduce the nitro group to monofunctional amine end groups.

Monohydroxy terminated poly(propylene oxide) oligomers of two different molecular weights (2000 g/mole and 5000 g/mole) were synthesized using anionic ring opening polymerization of the propylene oxide monomer with phenolate anion as the initiator in THF at 60°C, and terminating the polymerization after 48 hours with methanol. Phenol was dissolved in DMSO and a stoichiometric amount of K₂CO₃ was added, along with toluene used as the azeotrope. The reaction mixture was stirred for 5 hours at ~135°C, during which the water formed was stripped off, along with excess toluene. The entire solution containing the phenate ion was then transferred to a pressure reactor along, with dry THF and stoichiometric amounts of the propylene oxide monomer. The polymerization was allowed to proceed for a minimum of three days at 60°C after which the reaction was terminated by adding a large excess of methanol. Methanol and all unreacted propylene oxide monomer was stripped off under reduced pressure and the polymer was then dissolved in hexane, and decolorized using carbon black. The solvent was then stripped off to yield a light yellow viscous oil.

Hydroxy terminated poly(propylene oxide) was converted to the 4-nitro benzoate terminated poly(propylene oxide) by reacting it at room temperature with 4-nitro benzoylchloride in dry tetrahydrofuran (THF) as the solvent and pyridine as the acid acceptor. The nitro terminated poly(propylene oxide) solution was filtered to remove pyridinium hydrochloride salt. The solution was further rotovaped to remove the solvent, which resulted in a colorless dinitro terminated poly(propylene oxide) macromonomer. The molecular weight of the functionalized PO was assessed using ¹H NMR by integrating the aromatic protons of the end group with the aliphatic protons of the poly(propylene oxide). ¹H NMR of the mono nitro functionalized poly(propylene oxide) macromonomer is provided in Figure 4.3.1.2. The 4-amino benzoate terminated poly(propylene oxide)

was obtained by dissolving the mono-nitro terminated poly(propylene oxide) in THF and reducing the nitro groups on the macromonomer at room temperature with 50 psi pressure in a parr hydrogenation apparatus using Pearlman's catalyst. The reduction of the nitro groups to the respective diamine was also followed using ^1H NMR. Complete reduction of the nitro groups was observed after 48 hours. After reduction, the poly(propylene oxide) solution was filtered over celite and bentonite to obtain a clear solution. The filtrate was rotovaped resulting in a clear viscous solution of poly(propylene oxide) macromonomer. The molecular weight of the diamine terminated macromonomer was obtained by ^1H NMR and later verified by titrating the amine groups against 0.025N solution of HBr in acetic acid. These results are also tabulated in Table 4.3.1.1. The ^1H NMR of the amine functionalized poly(propylene oxide) macromonomer is provided in Figure 4.3.1.2.

Table 4.3.1.1 Characteristics of Monoamine Terminated Poly(propylene oxide) Oligomers

Sample	Molecular Weights (g/mole)	
	Target	From Titration
1	2000	2300
2	5000	5600

The copolymer synthesis involved the addition of solid PMDA to a solution of 3FDA and the monofunctional poly(propylene oxide) oligomer. The polymerization's were mediated in NMP at solid compositions of approximately 10-15 wt.%. The polymerization's were maintained at ambient temperatures for 24 hours, yielding viscous

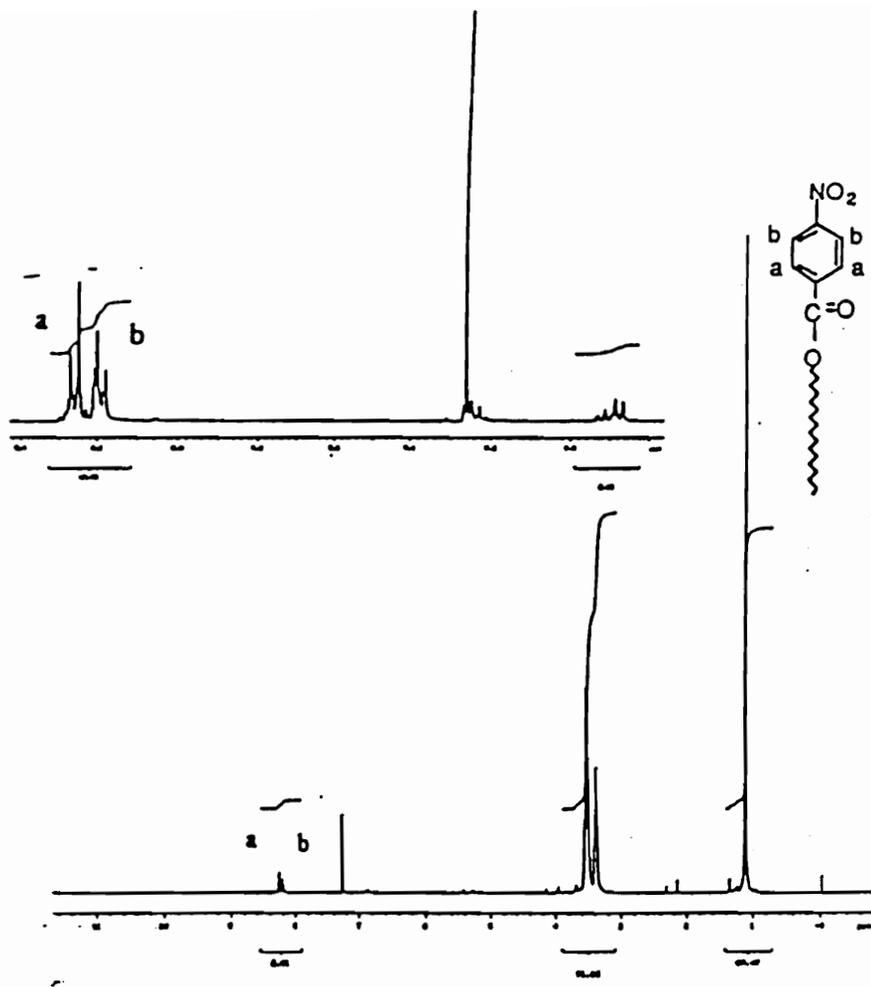


Figure 4.3.1.2 (a) ^1H NMR of the Nitro Functionalized Poly(propylene oxide) Macromonomer

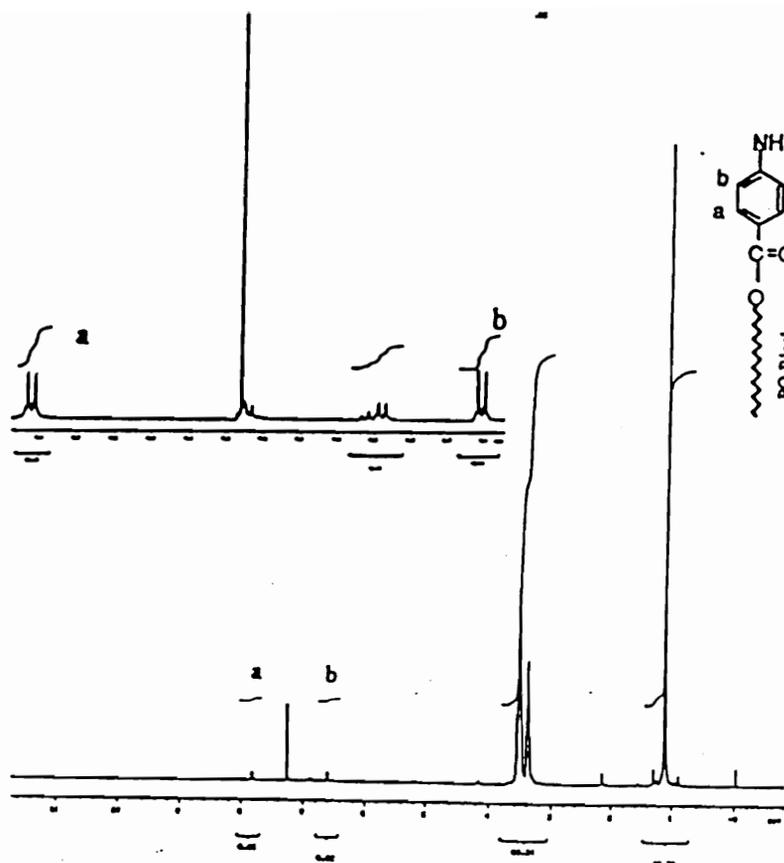


Figure 4.3.1.2 (b) ^1H NMR of the Amine Functionalized Poly(propylene oxide) Macromonomer

solutions of the target poly(amic acid). Imidization of the poly(amic acid) solutions was carried out directly through the chemical imidization technique. Chemical imidization was achieved with excess acetic anhydride and pyridine in 6-8 hours at 80°C.

The use of the preformed monofunctional, amine terminated poly(propylene oxide) macromonomer afforded an ABA triblock architecture, where the poly(propylene oxide) component terminated the growing polyimide chains, and consequently, comprised the terminal A blocks. The average molecular weight of the poly(propylene oxide) blocks was identical to that of the preformed oligomers, whereas the molecular weight of the imide block was controlled by the stoichiometric imbalance between the dianhydride and diamine, dictated by the propylene oxide block length and composition. The schematic representation of the copolymer synthesis is depicted in Figure 4.3.1.3.

A number of imide- poly(propylene oxide) copolymers were prepared and these are provided in Table 4.3.1.2 (samples 1-4). Two poly(propylene oxide) block lengths with composition of 15 and 25 wt.% were investigated as shown in Table 4.3.1.2. The poly(propylene oxide) compositions in the copolymer were deliberately maintained at low levels. It was anticipated that poly(propylene oxide) compositions of 15 wt.% or less would produce discrete domains of the thermally labile component in a high temperature polymer matrix, while the higher poly(propylene oxide) composition would approach cylindrical or a more interconnected type of structure. The composition of poly(propylene oxide) in the copolymer was assessed by both ¹H-NMR, by comparison of the integrated polyimide signal to that of the propylene oxide resonance's as depicted in Figure 4.3.1.4, and TGA, by measuring the weight retention after decomposition of the thermally labile block as shown in Figure 4.3.1.5. The composition of poly(propylene oxide) incorporated into the copolymer was comparable to that charged. The slight discrepancies was believed to result from the possible removal of the propylene oxide rich block copolymer. Also

Table 4.3.1.2 Characteristics of PMDA/3FDA Polyimide-Poly(propylene oxide)
Copolymers

Sample	Propylene Oxide Block length	Propylene Oxide Composition, wt.% Incorporation			Volume fraction of Propylene Oxide
		Charge	¹ H NMR	TGA	
1	2300	15	9.9	9	11
2	2300	25	23.0	22	27
3	5600	15	14.5	14	19
4	5600	25	24.0	23	26

shown in Table 4.3.1.2 is the volume fraction of poly(propylene oxide) incorporated in the copolymer with values ranging from 8 to 26%.

The processing window for the film and foam formation was established for these imide-propylene oxide copolymers by isolating and characterizing these polymers at various stages of processing. It is critical that the decomposition of the labile block occur substantially below the T_g of the polymer matrix. Furthermore, the film casting solvent (NMP) has to be effectively removed, without propylene oxide degradation, to minimize plasticization of the polyimide matrix, which, in turn would further narrow the processing window. In the case of the PMDA/3FDA polyimide, the ^1H NMR spectra and TGA spectrum of the sample cured at 300°C under nitrogen showed no detectable signs of NMP in the film. Since poly(propylene oxide) is stable up to 300°C in nitrogen atmosphere, samples cured to this temperature to remove the casting solvent should retain their propylene oxide composition in the copolymers. With this in mind films of these materials were prepared by casting solutions of the copolymer onto a glass plate and curing under nitrogen up to 300°C for 1 hour to afford clear tough films. Shown in Figure 4.3.1.4 is the ^1H NMR spectra of a redissolved film of copolymer which has been cast from NMP and cured to 300°C for 1 hour. It can be observed clearly that complete removal of NMP has been achieved with minimal loss in the propylene oxide composition.

The dynamic mechanical analysis for the PMDA/3FDA polyimide-poly(propylene oxide) triblock copolymers are shown in Figure 4.3.1.6. The copolymers 1 to 5 exhibited two transitions characteristic of a microphase separated morphology. The transition occurring near -60°C is in the region of the expected T_g of -70°C ²⁰⁵ for poly(propylene oxide). The copolymers comprised of the lower propylene oxide block lengths showed damping peaks that are rather diffuse and broad, suggesting significant amount of interfacial mixing. Conversely, in most cases, the copolymers with the higher propylene oxide block lengths showed less broad damping peaks, suggesting that the interfacial

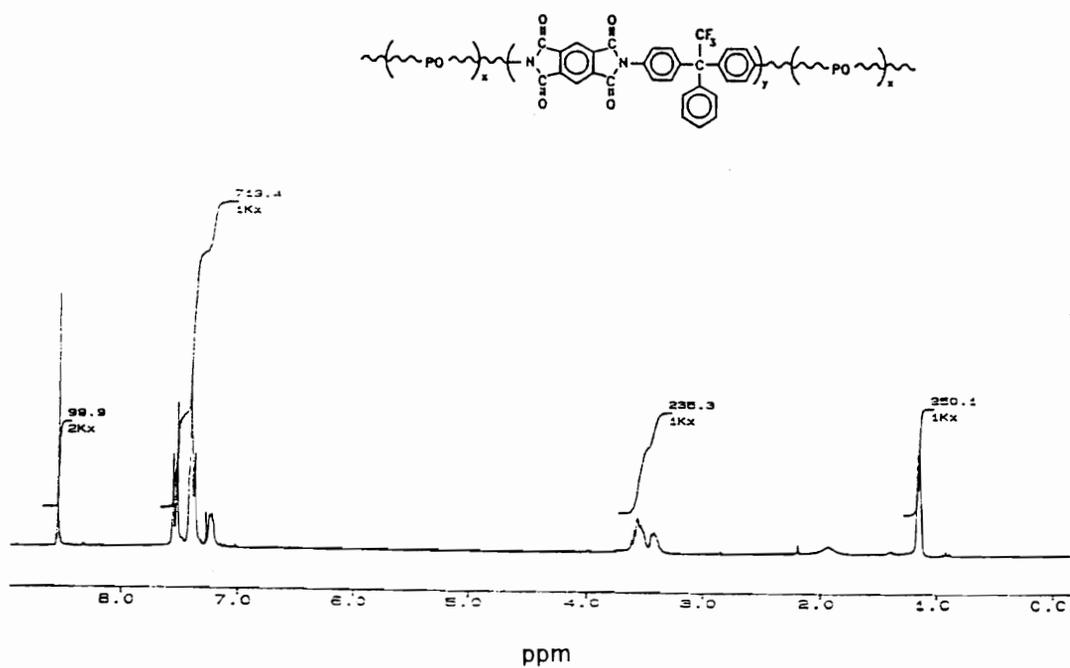


Figure 4.3.1.4 ¹H NMR Spectra of PMDA/3FDA/PO Block Copolymer Film (cast from NMP and cured to 300°C for 1 hour)

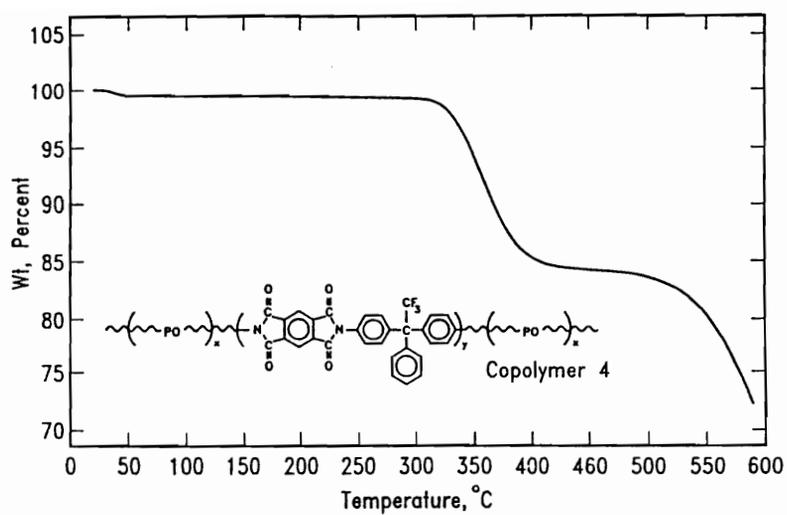


Figure 4.3.1.5 Dynamic TGA Thermogram of PMDA/3FDA/PO (15 wt% PO) Block Copolymer Film (cast from NMP and cured to 300°C for 1 hour (Heating rate 10°C/min))

mixing is less. The transition temperature of the polyimide block was essentially independent of the propylene oxide block lengths.

The generation of the foam structure was accomplished through decomposing the poly(propylene oxide) by subjecting the copolymer films to a thermal treatment in air. Mild temperatures were employed to decompose the propylene oxide coblock as the degradation of the poly(propylene oxide) was expected to be considerably faster than the diffusion of the low molecular weight by-products, hence, plasticization of the polyimide block could occur resulting in the possible collapse of the foamed structure. Foam formation was accomplished by first heating the copolymer at 240°C in air for 6 hours. Figure 4.3.1.7 shows the isothermal weight loss as a function of the propylene oxide component. Once subjected to this treatment, the samples were redissolved and characterized using ^1H NMR. Although isothermal TGA experiments indicated quantitative degradation of the labile block at 240°C, NMR showed about 5% of the labile block remaining. Hence, the samples were post-treated at 300°C for 1 to 2 hours to complete the decomposition of the labile block. The ^1H NMR of the post treated sample is provided in Figure 4.3.1.8, clearly indicating quantitative removal of the labile block under these conditions. Thereafter, foam formation was achieved on the remaining samples by heating the copolymers to 240°C for 6 hours followed by a post bake at 300°C for 2 hours in an air atmosphere.

The density values of the foamed copolymers, together with the polyimide homopolymers, are provided in Table 4.3.1.3 and clearly shows the foam formation. The density value for the PMDA/3FDA homopolyimide was found to be 1.34 g cm^{-3} , while most of the copolymers ranged from 1.09 to 1.27, which is approximately 82 to 91% of the control. This is consistent with 9 to 18 % of the film being occupied by voids. From this data (comparison of Tables 4.3.1.2 and 4.3.1.3) it appears that the volume fraction of voids or the porosity is somewhat lower than the volume fraction of the propylene oxide in the copolymer. Thus, the efficiency of the foam formation, although high, is not

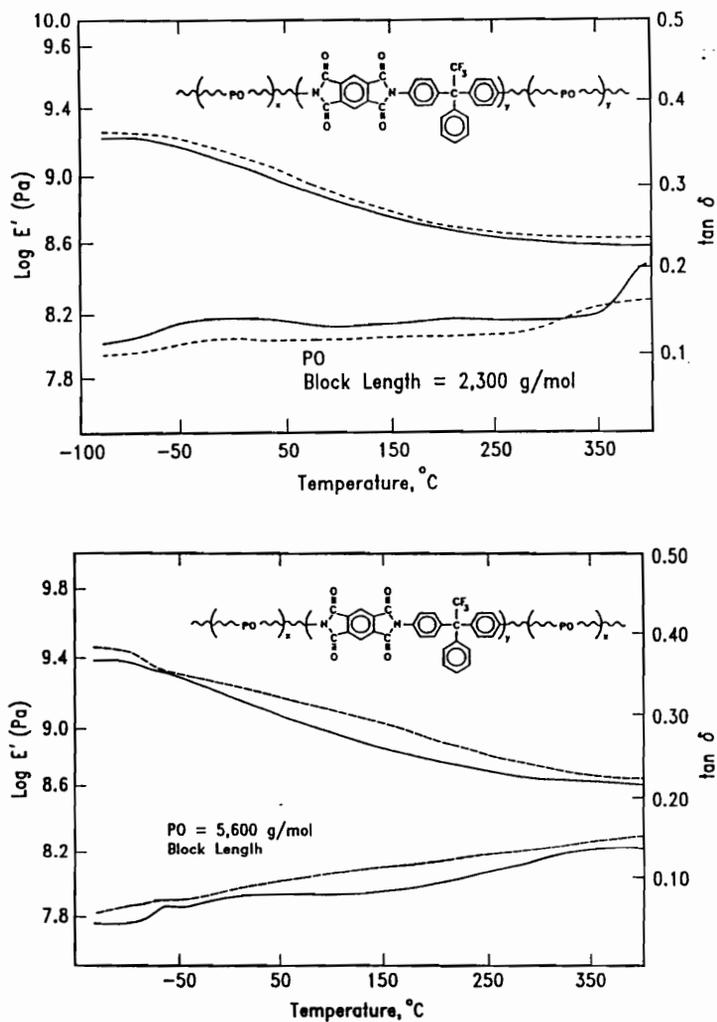


Figure 4.3.1.6 Dynamic Mechanical Analysis for the PMDA/3FDA Polyimide-Poly(propylene oxide) Triblock Copolymers [a) 15 and 25 wt. % of poly(propylene oxide) mol.wt. 2300 g/ mole, b) 15 and 25 wt. % of poly(propylene oxide) mol.wt. 5600 g/ mole]

Table 4.3.1.3 Characteristics of PMDA/3FDA Polyimide Foams

Sample	Density (g/cc)	Volume Fraction of Voids (%)
PMDA/3FDA Homopolymer	1.34	-
1	1.22	9
2	1.13	16
3	1.17	13
4	1.10	18

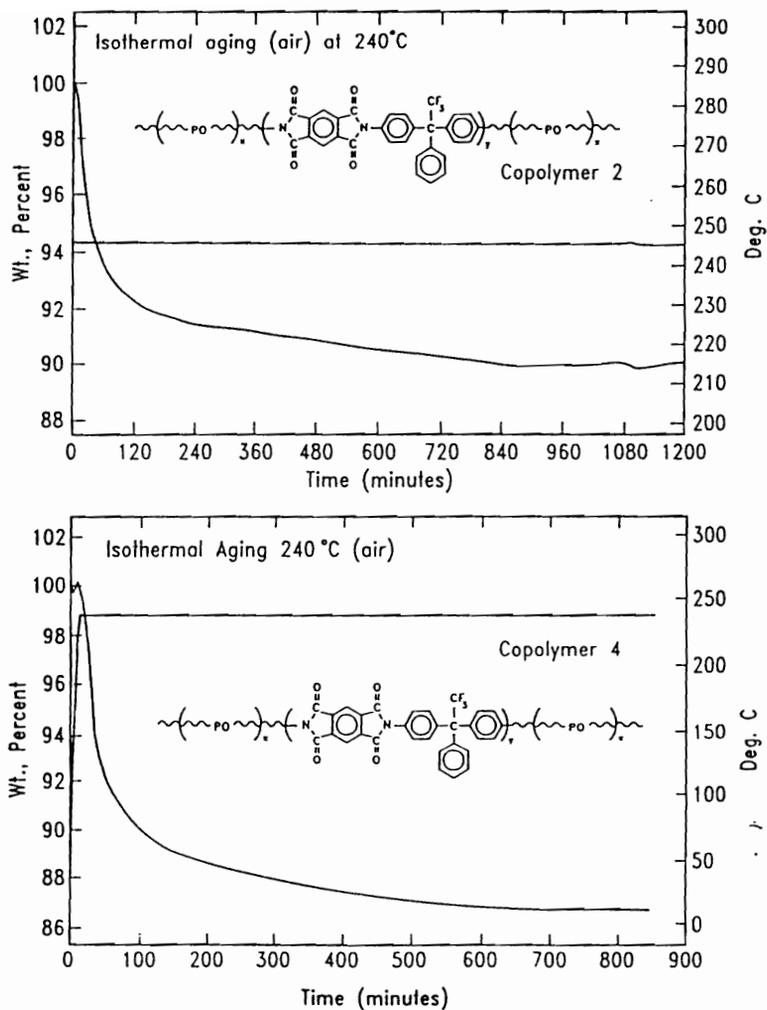


Figure 4.3.1.7 Isothermal TGA Thermograms for Copolymers 1 and 3 at 240°C in air

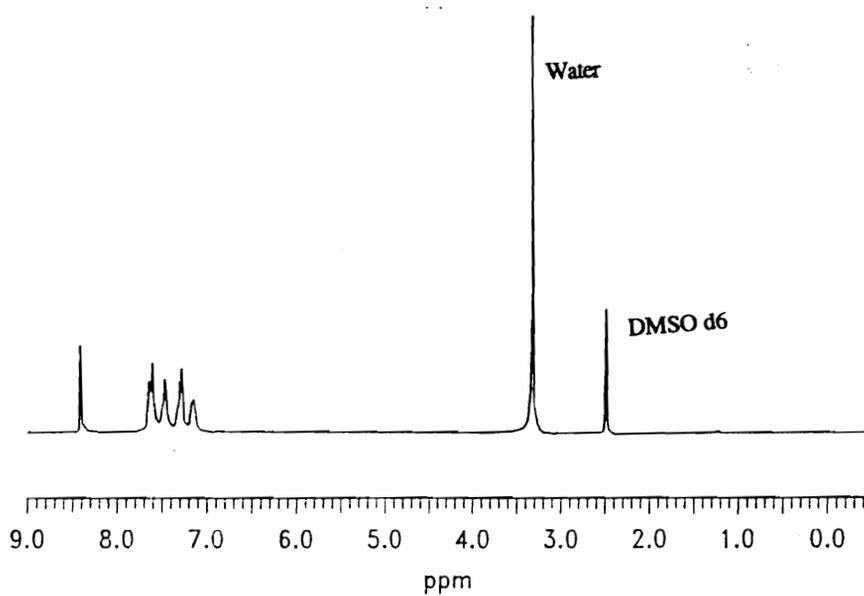


Figure 4.3.1.8 ^1H NMR of Copolymer 1 post treated at 300°C for 2 hours in air

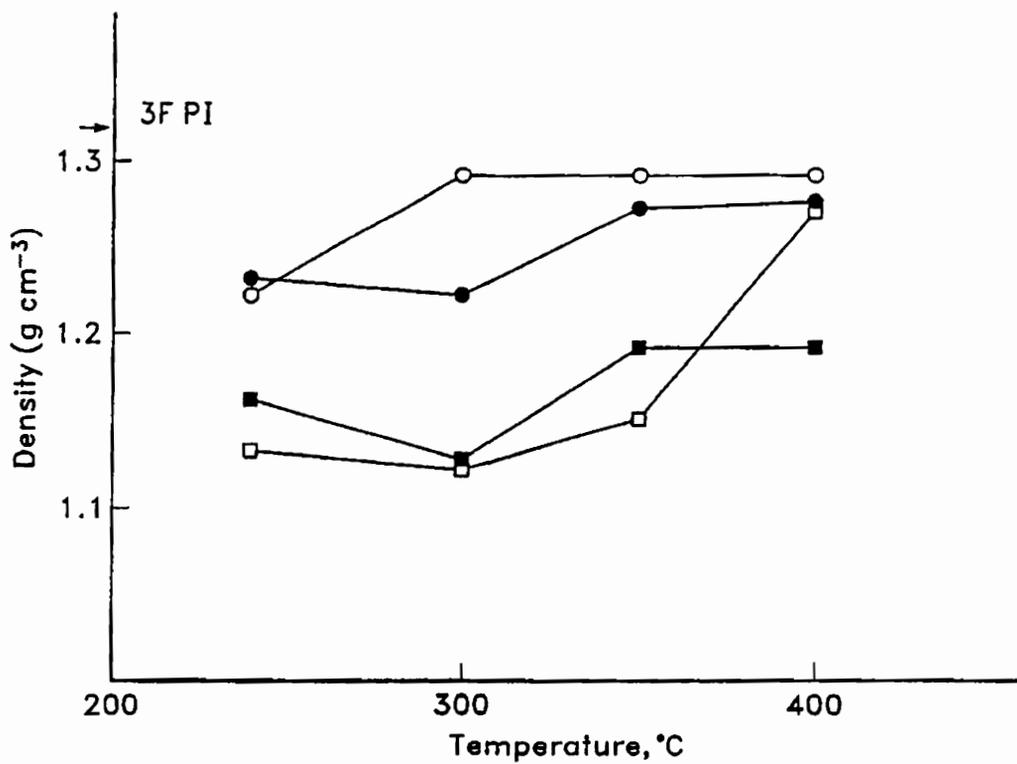


Figure 4.3.1.9 Room Temperature Density as a Function of Curing Temperature for Copolymers 1 (●), 2 (○), 3 (■), 4 (□)

quantitative. The high T_g of the polyimide allowed the investigation of higher foaming temperatures on the density as a means of improving the foaming efficiency. Several cure temperatures were investigated including 240, 300, 350 and 400°C, and these results are provided in Figure 4.3.1.9. Samples were held at the respective temperatures for 1.5 hours, except for the sample cured at 240°C, which was held at that temperature for 6 hours. As expected, a further drop in the density was observed as the foaming temperatures were increased from 240 to 300°C. Foaming temperatures of 350 and 400°C produced foams with higher density, consistent with partial collapse. Presumably the partial collapse in the structure results from the cooperative segmental mobility imparted in the system as the temperature, approaches the glass transition temperatures of the homopolyimide. Consequently, the optimum foaming temperature, as determined by $^1\text{H-NMR}$ and density measurements, appears to be 300°C. However, it should be pointed out that even at the higher cure temperature the foam structure is maintained to some extent.

In order to study the thermal stability of PMDA/3FDA based foams, samples of each material was held for 1 hour at several temperatures and their density was measured. Over the temperature range studied (240 - 400°C), the density appears to be essentially invariant for the foams derived from the copolymers with the higher molecular weight propylene oxide block. However, the foams derived from the copolymers with the low molecular weight propylene oxide block showed a slight increase in density between 350 and 400°C, as indicated in Figure 4.3.1.10. Thermal mechanical analysis also used to study the stability of the cellular structure as a function of temperature. In these experiments, a small tensile deformation was placed on the sample and was then heated. The deformation or displacement is plotted as a function of temperature for both the foamed (copolymer 4) and the homo polymers as shown in Figure 4.3.1.11. Initially, the foam showed a similar displacement / temperature profile to that of the homopolymer. However,

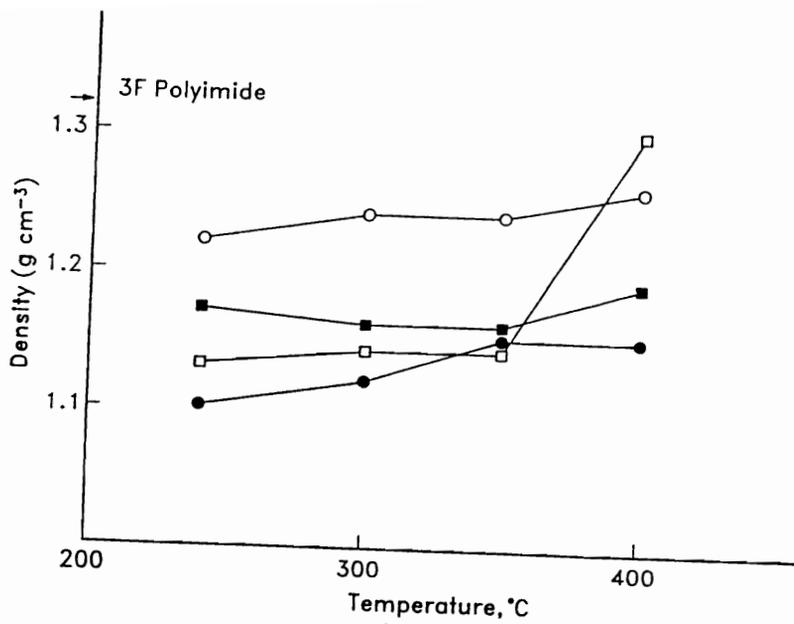


Figure 4.3.1.10 Densities of the PMDA/3FDA Based Foams from Copolymers 1(●), 2(○), 3(■) and 4(□) held for 1 hour at several temperatures

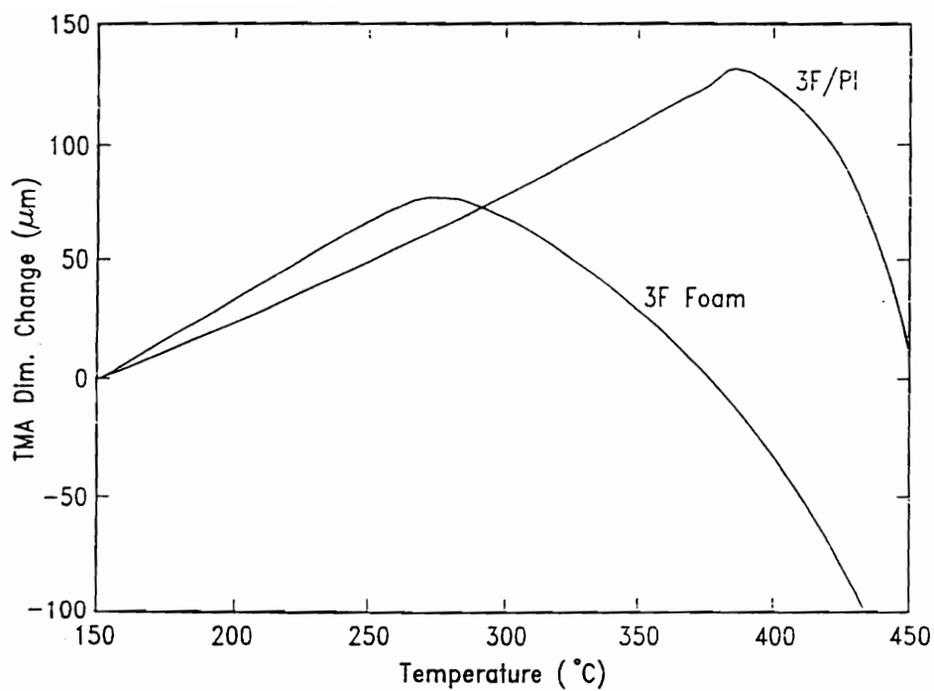


Figure 4.3.1.11 Displacement as a Function of Temperature for PMDA / 3FDA Polyimide and PMDA/3FDA Polyimide Foam Copolymer 4

at approximately 300°C a large change in slope was observed which is, consistent with the minor contraction of the sample. Thus, TMA also reveals that the foamed materials began to collapse above 300°C, consistent with the density measurements.

Even though density measurements proved that foam had been successfully achieved, no information was provided on the size of the pores. To address this issue, transmission electron microscopy (TEM) was used. Figure 4.3.1.12 shows the TEM of a typical microtomed section of copolymer 4 after decomposition of the propylene oxide coblock. The dark regions in the micrograph correspond to the polyimide matrix. From the micrograph, it is evident that a porous structure is obtained, with pores having an average diameter of 8-10 nm. It is also clear that little interconnectivity between the pores and the desired “ Closed Cell ” morphology has been achieved.

Thus, foam formation was achieved using the poly(propylene oxide) as the labile block and these above results proved that successful nano foam formation was possible with the use of high T_g amorphous polyimides, such as the PMDA/3FDA based system. However, it is worth mentioning that volume fraction of voids in each case does not correspond to the volume fraction of the poly(propylene oxide) in the initial copolymer. Moreover, an inherent problem of the triblock copolymer approach in general is that monoamine terminated poly(propylene oxide) is used with the monomers of the polyimide to obtain a copolymer having an ABA triblock architecture, where A corresponds to the poly(propylene oxide) block. Since the monoamine terminated poly(propylene oxide) would act as an endcapper, the molecular weight of the thermally stable polyimide block was dependent on the poly(propylene oxide) composition. Calculation of the molecular weight of the polyimide B block based on the amount of endcapper used, indicated that the molecular weight should range approximately from theoretical molecular weights of 15000 g/mole for 25 wt.% incorporation of 2300 g/mole poly(propylene oxide) oligomer to 40,000 g/mole for 25wt.% incorporation of 5600 g/mole oligomer, as calculated from

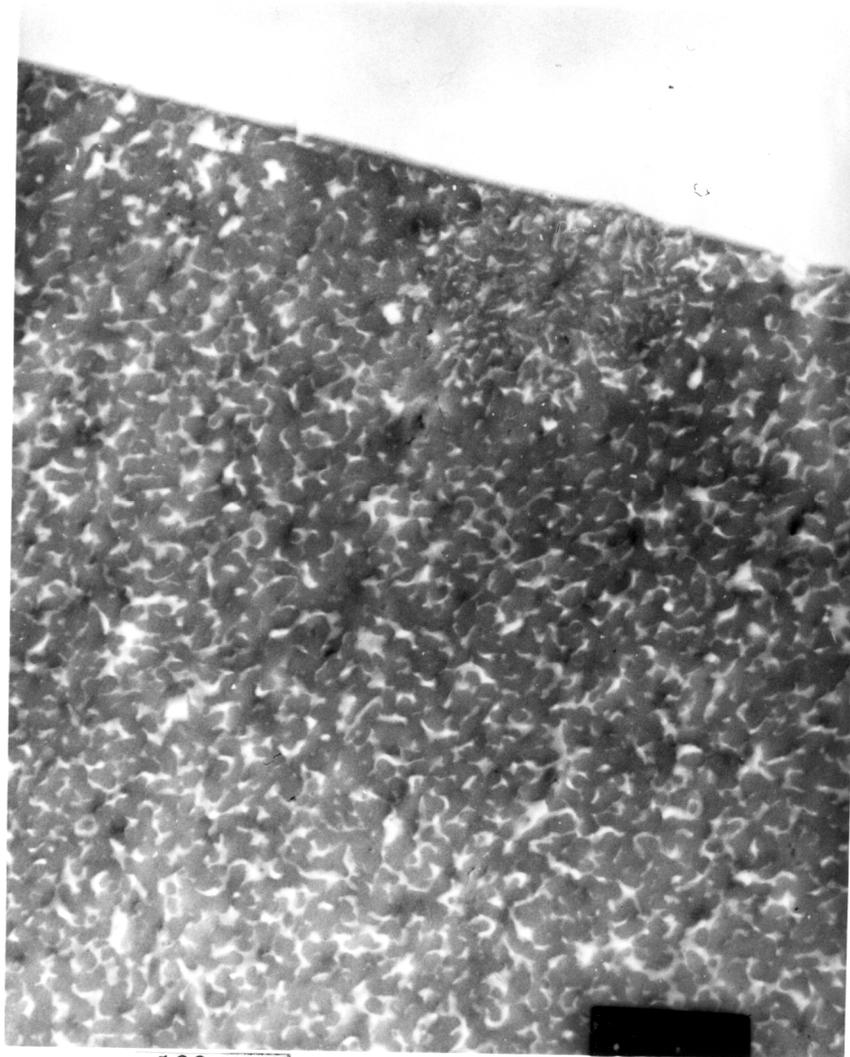


Figure 4.3.1.12 Transmission Electron Microscopy of Copolymer 4 after the PO was degraded yielding the nanofoam structure (187, 000 X)

Carother's equation for the number average degree of polymerization. Not only due to the inherent nature of foamed materials to have lower mechanical properties compared to unfoamed polymer, but these reduced mechanical properties (e.g. toughness) could also result from the lower calculated molecular weight of the polyimide backbone, especially for higher percent incorporation of the lower molecular weight poly(propylene oxide) oligomers. Moreover, TEM indicates the presence of a variety of pore sizes and shapes, presumably arising from the degradation of the poly(propylene oxide).

An alternative to the block copolymer approach would be the graft copolymer approach. Diamine terminated poly(propylene oxide) was required to generate a graft copolymer, which when copolymerized with the polyimide monomers, should not restrict the total molecular weight of the polyimide backbone. Hence, no restriction in the molecular weight growth of the backbone is expected occur via this approach. This could result in improved mechanical properties of the foamed polyimide, when compared to that of the material obtained from the block copolymer approach. Thus, in the case of graft systems, the thermally stable polyimide block would act as the backbone to which the thermally labile block would be randomly grafted. It was felt that this approach might also result in pores with better uniformity with respect to size and shape, when compared to those obtained from block copolymers. The next section discusses of the nanofoams prepared from polyimide-poly(propylene oxide) graft copolymers.

4.3.2 Synthesis and characterization of polyimide foams from PMDA/3FDA based polyimide-poly(propylene oxide) graft copolymers

PMDA/3FDA based polyimide-poly(propylene oxide) graft copolymers were also synthesized via the same two-step synthetic methodology, used for the block copolymers. In the first step, grafted poly(amic acid) was synthesized, which was followed by chemically imidizing the respective poly(amic acid) solution using pyridine and acetic anhydride to obtain the polyimide graft copolymers

In order to synthesize the graft copolymers, diamine terminated poly(propylene oxide) had to be synthesized. Monohydroxy poly(propylene oxide) of 3 different molecular weights (3000, 4000 and 8000 g/mole) were synthesized using anionic ring opening polymerization of propylene oxide monomer, as described earlier. It was then derivatized into diamino benzoate terminated oligomers. The resulting polyimide copolymerization was accomplished via a two-step process by first reacting the monohydroxy terminated poly(propylene oxide) oligomer with 3,5 dinitrobenzoyl chloride in dry tetrahydrofuran solvent containing pyridine as the catalyst and acid acceptor. After the reaction, the solution was filtered to remove pyridine hydrochloride salt and the filtrate was further rotovaped to remove the solvent. This produced a clear viscous dinitro terminated poly(propylene oxide) oligomer. The dinitro terminated poly(propylene oxide) was characterized using ^1H NMR to confirm that complete conversion of the hydroxy group to the dinitro benzoate functionalized poly(propylene oxide) was achieved. The second step involved the hydrogenation of the dinitro benzoate terminated poly(propylene oxide) with Pearlman's catalyst (palladium hydroxide on carbon) and hydrogen in tetrahydrofuran to the respective diamino benzoate functionality. The molecular weight of the amino benzoate functionalized poly(propylene oxide) was characterized using both ^1H NMR and standard potentiometric titration of the amine end groups against standardized solution of HBr in acetic acid. These results are shown in Table 4.3.2.1.

Table 4.3.2.1 Characterization of Diamino Benzoate Terminated Poly(propylene oxide) Oligomers

Sample	Molecular Weights (g/ mole)		
	Target	¹ H NMR ³	From Titrations ⁴
1	3000	4900	3100
2	4000	4500	4100
3	8000	8800	7900

³based on diamine terminated PO; ⁴amine end groups titrated against HBr/AcOH mixture

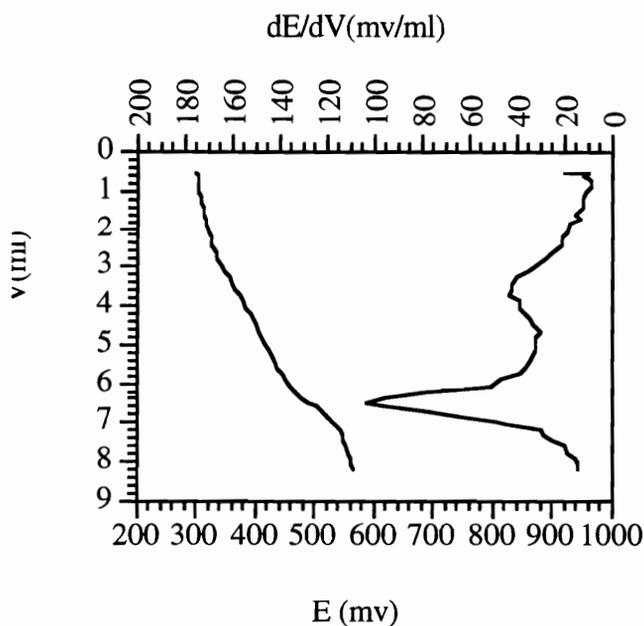


Figure 4.3.2.1 Potentiometric Titration Profile of the Amine Functionalized PO(mol.wt = 8000g / mole)

The potentiometric titration profile of the amine functionalized poly(propylene oxide)(mol.wt = 8000g / mole) is shown in Figure 4.3.2.1. The ^1H NMR of the poly(propylene oxide) (mol wt = 8000g/mole) oligomer functionalized with dinitro and with diamine functional groups is shown in Figure 4.3.2.2a and 4.3.2.2b, respectively.

The copolymer synthesis involved the addition of the solid PMDA to a solution of 3FDA and the diamine functionalized poly(propylene oxide) oligomer. The reaction scheme for the copolymer synthesis is provided in Figure 4.3.2.3. The polymerization's were carried out in NMP at solid compositions of approximately 15 wt%. Polymerization's at ambient temperature for 24 hours yielded viscous solutions of the target poly(amic acids). Imidization of the poly(amic acid) solutions was carried out directly and was accomplished by adding excess acetic anhydride and pyridine, and further stirring the reaction for 6-8 hours at 80°C. The use of the diamine terminated poly(propylene oxide) oligomers afforded graft copolymers, of the poly(propylene oxide) macromonomers grafted on to the polyimide main chain. Using this approach very high molecular weights of the polyimide backbone can be achieved, irrespective of the copolymer composition, while the average molecular weight of the propylene oxide blocks is identical to that of the preformed oligomers.

A number of imide - propylene oxide copolymers were prepared. Two propylene oxide oligomers with compositions of 15 and 25 wt% were investigated, analogous to the case of the block copolymers, and these results are provided in Table 4.3.2.2. The propylene oxide composition in the copolymer was again maintained at a low level in order to obtain discrete domains of the thermally labile component in a high temperature polymer matrix. Any unreacted PO oligomers were completely removed by stirring of the precipitated copolymer overnight in hot methanol. The composition of the propylene oxide in the copolymer was assessed by both ^1H -NMR, comparing the integrated aromatic

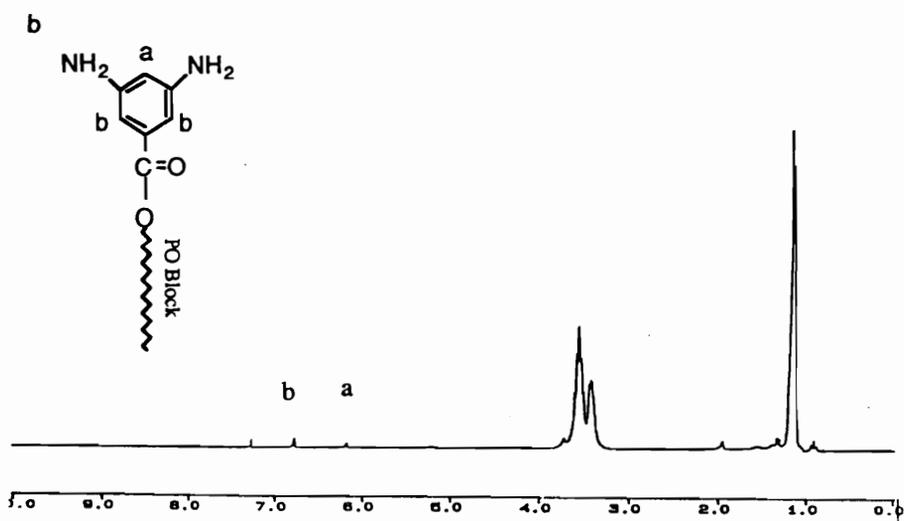
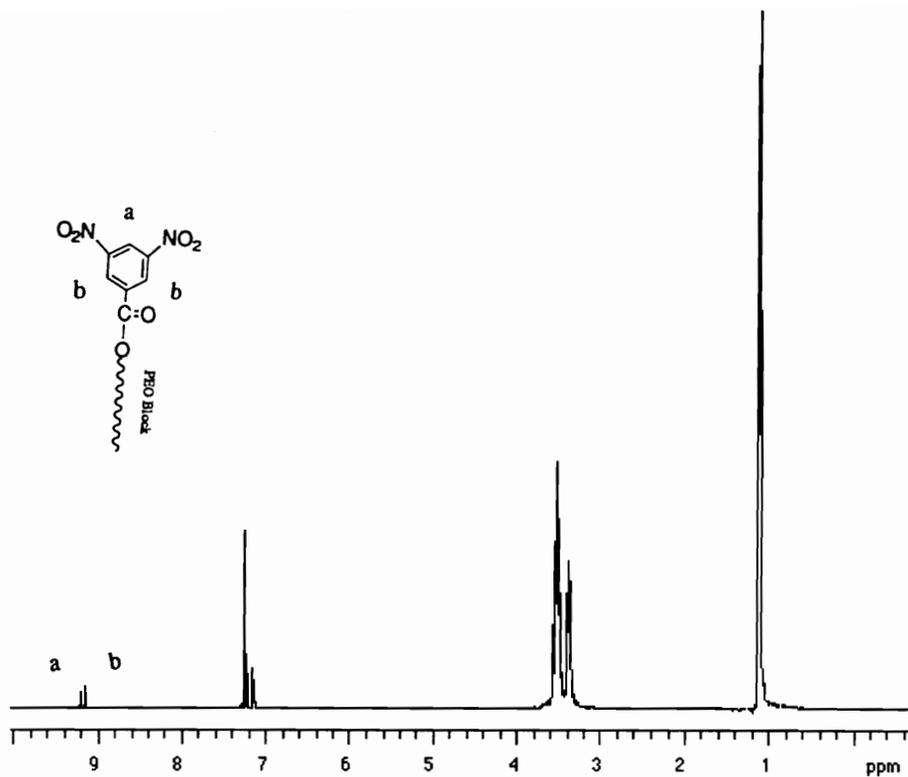


Figure 4.3.2.2: a and b are ^1H NMR Spectrums of the PO(mol wt = 8000g/mole) Oligomer Functionalized with Dinitro and with Diamine Functional Groups respectively.

protons of the polyimide to that of the aliphatic protons of the propylene oxide as shown in Figure 4.3.2.4, and by TGA, by measuring the weight retention after decomposition of the thermally labile block, as shown in Figure 4.3.2.5. The composition of propylene oxide incorporation into the copolymer was comparable to that charged, as shown in Table 4.3.2.2.

The processing window for film and foam formation has been established for PMDA / 3FDA / PO copolymers using ^1H NMR, TGA, and dynamic mechanical measurements of the block copolymers. In order to prepare polyimide films, samples of PMDA / 3FDA / PO copolymers were dissolved in NMP and cast on to a glass plate. The glass plate was gradually heated at a rate of $5^\circ\text{C} / \text{min}$ to 300°C and held there for 1 hour under nitrogen atmosphere. This resulted in a slightly hazy, tough polyimide - poly(propylene oxide) copolymer film. The ^1H NMR spectra of the samples cured at 300°C showed no detectable traces of the solvent (NMP). Also, integration of the polyimide aromatic protons against those of the aliphatic protons of propylene oxide indicated no detectable loss of the thermally labile PO under this condition. The ^1H NMR spectra of the of copolymer containing 25 wt% of PO (mol wt = 8000 g/mole) that was cast from NMP and cured to 300°C for 1 hour is also shown in Figure 4.3.2.4b. It was demonstrated that complete removal of the solvent NMP was achieved with minimal loss of poly(propylene oxide).

The dynamic mechanical results for the imide - propylene oxide graft copolymers were performed for all the samples under nitrogen atmosphere. Copolymers (1 - 5) exhibited two transitions, like the block copolymers, which is characteristic of a microphase separated morphology. The low temperature transition occurring near -60°C is consistent with the poly(propylene oxide) oligomers glass transition temperature, and a higher temperature transition corresponding to that of the polyimide block, occurring near 400°C . The higher temperature transition was observed to be essentially independent of the

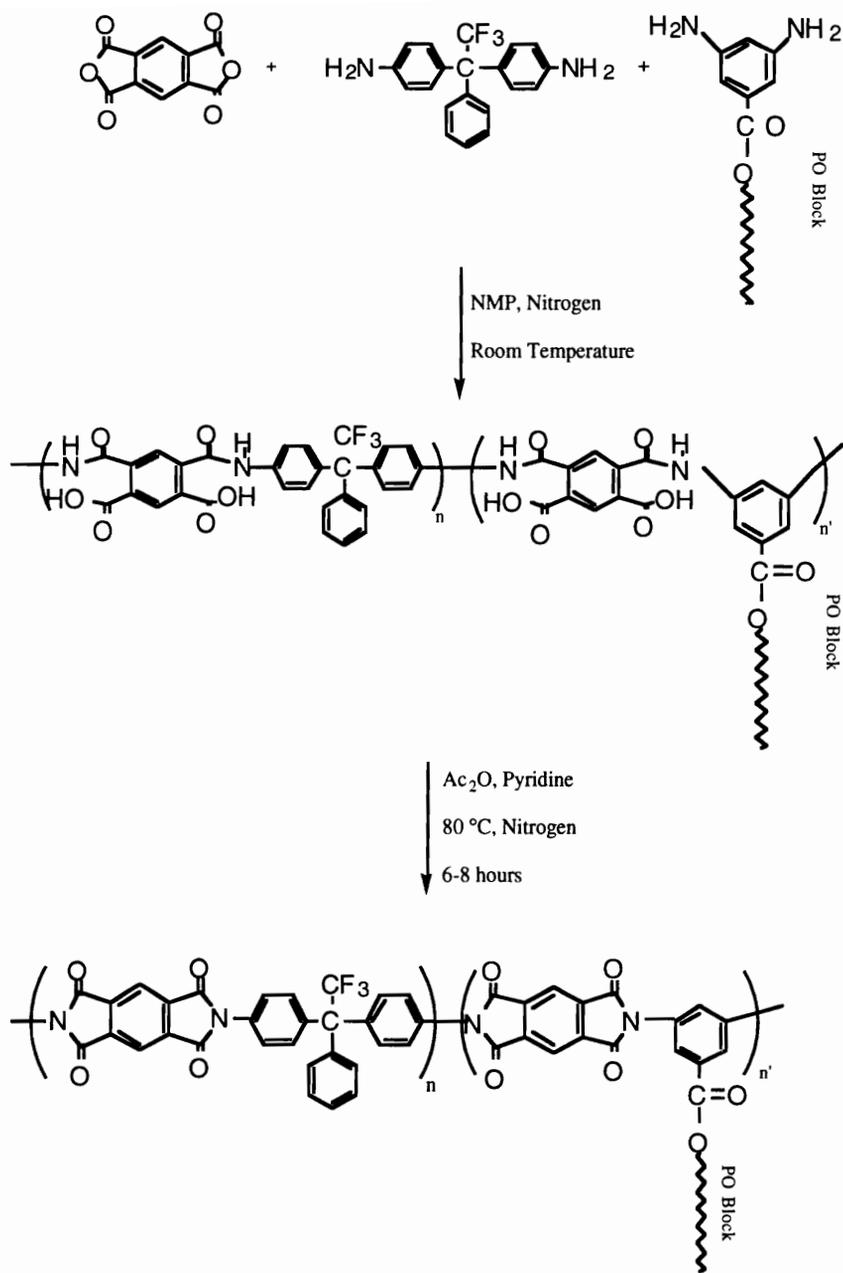


Figure 4.3.2.3 Synthesis of PMDA/3FDA/PO Graft Copolymers

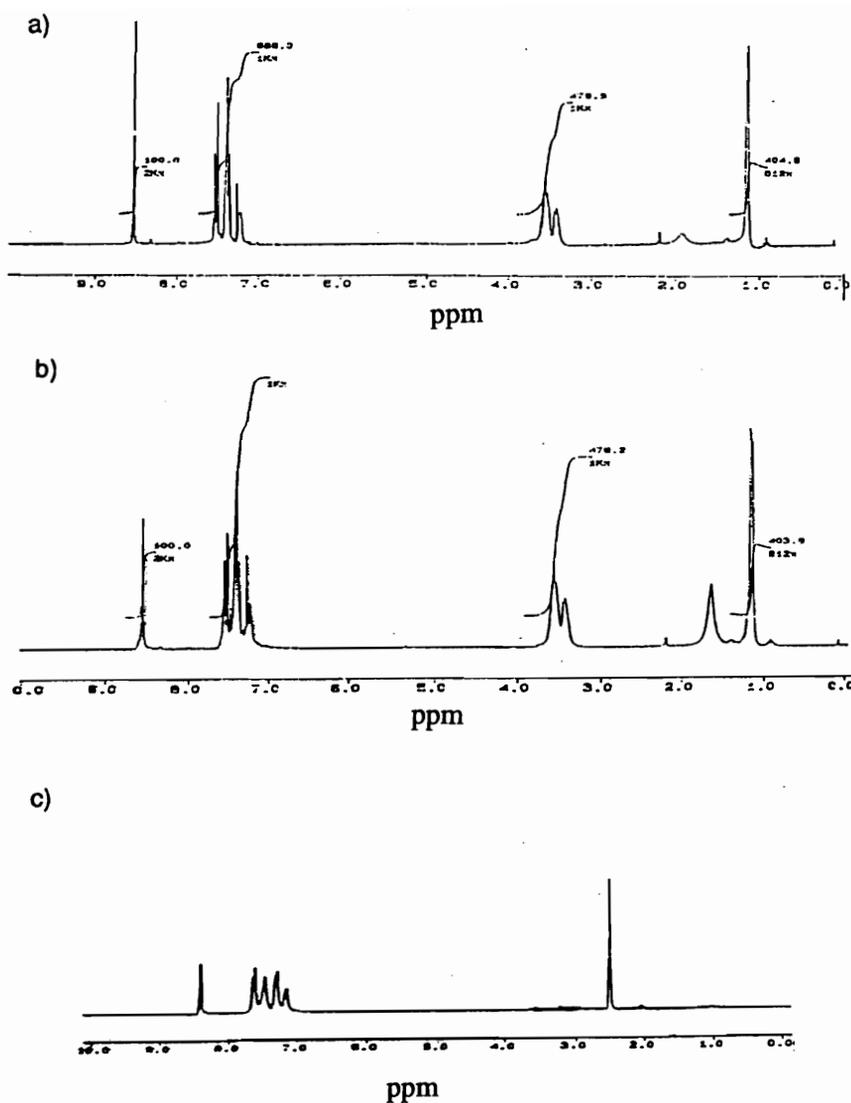


Figure 4.3.2.4 ^1H NMR spectra of PMDA/3FDA/PO Graft Copolymer (mol. wt. of PO 8000 g/mole, wt% = 25%), a) as prepared sample, b) of film cast from NMP and cured at 300°C in nitrogen, and c) of film foamed at 300°C for 10 hours

Table 4.3.2.2 Characteristics of PMDA/3FDA/PO Graft Copolymers

Sample	PO Mol. Wt. (g/mole)	Weight % incorporation of poly(propylene oxide)(PO)			Volume Fraction of PO in copolymer
		Target	From ¹ H NMR	From TGA	
1	3100	25	24.9	24	30.09
2	3100	15	15.1	14.3	19.06
3	4100	25	24.5	24	28.5
4	8000	25	21.9	22.1	26.7
5	8000	15	15.7	16	19.7

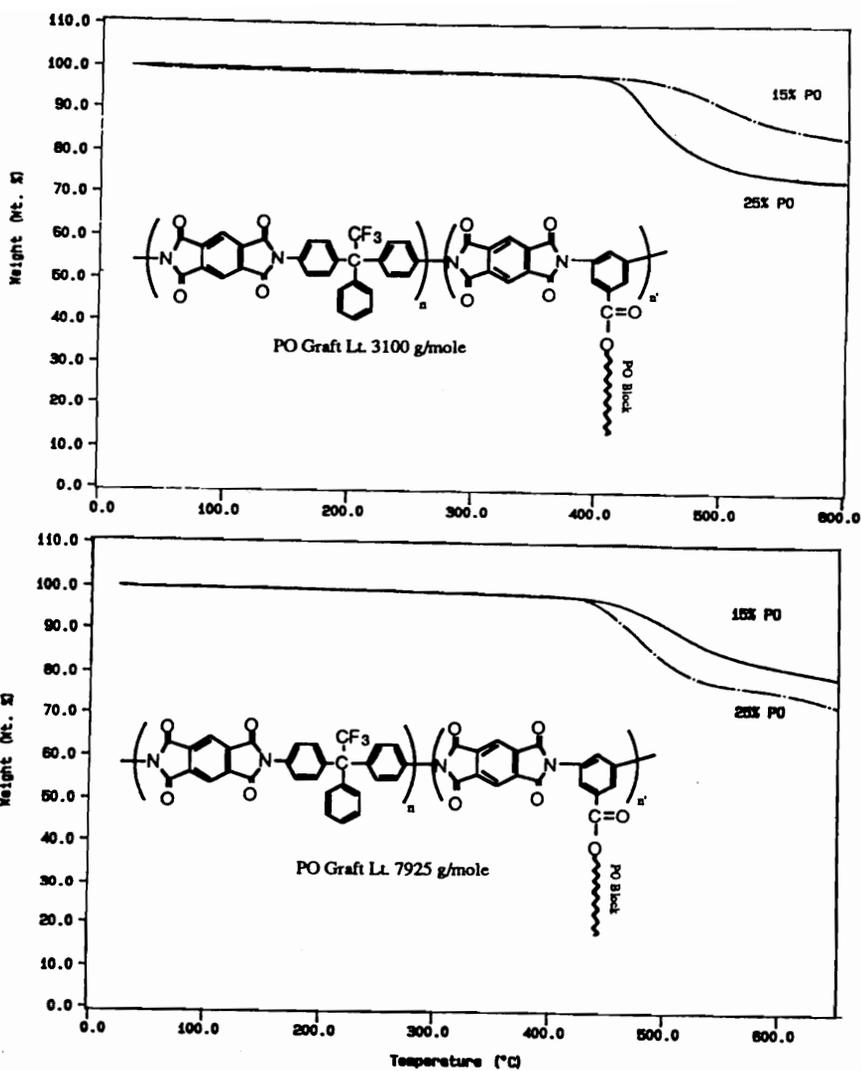


Figure 4.3.2.5 Dynamic TGA Thermogram of PMDA/3FDA/PO Graft Copolymer films (cast from NMP and cured to 300°C for 1 hour (Heating rate 10°C/min)), a) TGA thermogram of Copolymers 1 and 2, and b) TGA spectrums of Copolymers 4 and 5

propylene oxide block length. The copolymers comprised of the lower molecular weight poly(propylene oxide) grafts (PO mol. wts. 3100 and 4100 g/mol) exhibited a small and diffused damping peak rather than a broad peak, observed in the case of the block copolymers, indicating a significant amount of interfacial mixing. However, the copolymers having higher molecular weight PO grafts at higher compositions demonstrated a sharper damping peak, suggesting a sharper phase boundary. DMA spectra obtained for copolymers 1, 3 and 4 containing the same wt.% (25) of PO, but of varying block length, is provided in Figure 4.3.2.6.

Isothermal TGA experiments in air were performed in order to define the foaming temperatures for these copolymers. Based on the results obtained from the block copolymers isothermal experiments were performed at 240 and 270°C for copolymers 1, 2, and 3, while 240, 270 and 300°C were used for copolymers 4 and 5. Copolymers 1, 2, and 3 exhibited near quantitative decomposition of the poly(propylene oxide) component under an isothermal TGA experiment in air at 270°C. A similar experiment, performed on copolymer 4, however did not exhibit near quantitative decomposition of the poly(propylene oxide) component at 270°C, even after 12 hours in air. Further isothermal experiments performed on the same copolymer in air at 300°C exhibited quantitative decomposition of the PO component. Hence, based on the above isothermal experiments, the foaming temperature for copolymers 1, 2, and 3 was determined to be 270°C and for copolymers 4 and 5 the foaming temperature was fixed as 300°C in air. Shown in Figure 4.3.2.7 and 4.3.2.8 shows the plots of isothermal weight loss as a function of time for copolymer 1 performed at 240°C and 270°C, and for copolymer 4, performed at 270°C and 300°C respectively.

In order to foam the copolymers, films of the respective copolymers were subjected to the preassigned temperatures in air for a period of 10 hours. At the end of the foaming process, part of the foamed sample were taken and redissolved in deuterated DMSO to

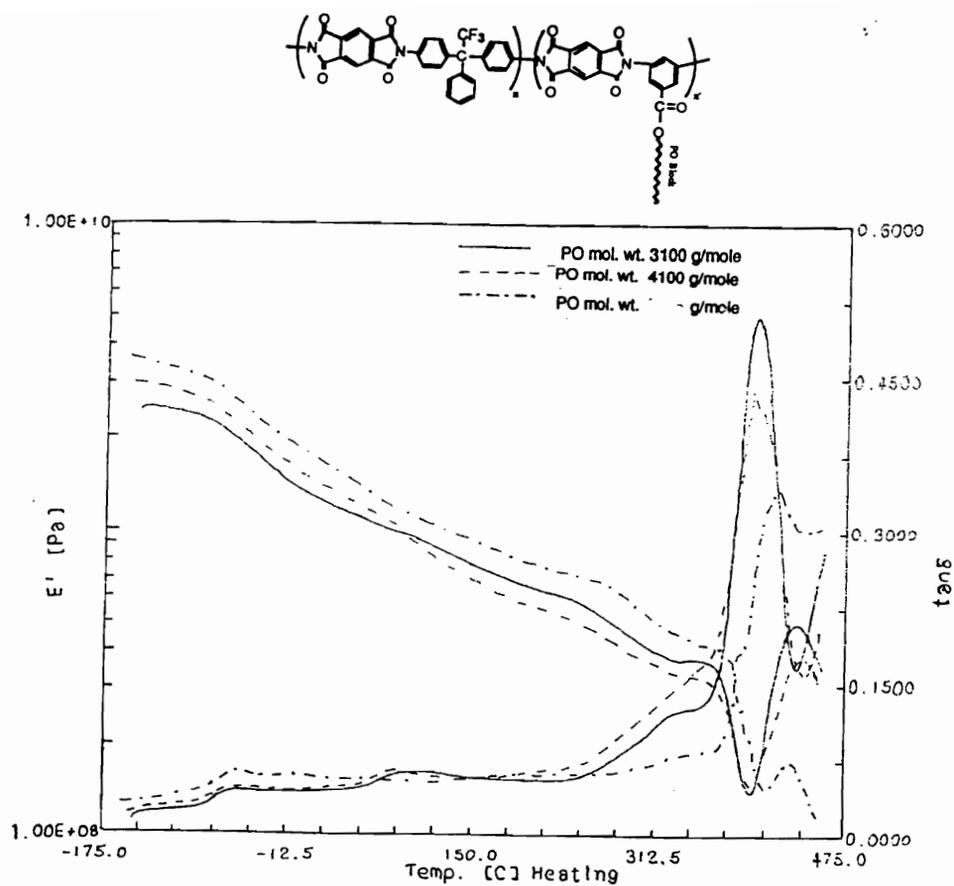


Figure 4.3.2.6 Dynamic Mechanical Analysis of the PMDA/3FDA/PO Graft Copolymers ((Wt.% of PO = 25) the effect of block length on the storage modulus and loss tangent)

obtain ^1H - NMR of the sample. The ^1H NMR spectrum clearly indicated quantitative removal of the propylene oxide coblock as shown in Figure 4.3.2.4 c.

Density measurements were performed on the foamed polyimide copolymers and compared to those of the homopolymer. These results are provided in Table 4.3.2.3, clearly lists substantially lower density values for all of the foamed copolymers. These densities ranged from 1.09 to 1.17, which is consistent with void amount of 12 to 18 % for the films. These results are quite consistent with the results that were earlier observed in for the PMDA/3FDA based triblock copolymers.

Thermal stability of the foams was investigated by measuring the density change after maintaining each of the foamed samples at a set temperature for 1 hour under nitrogen atmosphere . The samples were held at 300, 350 and 400°C, respectively, and the plot of room temperature density as a function of aging temperature for the foamed samples is shown in Figure 4.3.2.9. Over the temperature range studied (240 - 400°C), foam density appears to increase between 350 and 400°C, thus indicating partial collapse of the foam as the T_g of the polyimide phase is approached.

TEM was performed on the polyimide - PO graft copolymer after the decomposition of the propylene oxide block. These results are provided in Figure 4.3.2.10, Figure 4.3.2.11 and Figure 4.3.2.12. The dark regions in the micrograph correspond to the polyimide matrix. From the micrograph, it is evident that a micro porous structure was obtained. It is also clear that discrete pores with little to no interconnectivity between the pores was achieved, as in the case of the block copolymers. However, the pores were more homogenous throughout the film, in the case of foams obtained from copolymers 1 to 3. This may be because of the moderate poly(propylene oxide) graft lengths, while much higher graft lengths, such as in the 8000 g/mole sample, pores were observed to be much larger and less

Table 4.3.2.3 Characteristics of PMDA/3FDA/PO Graft Copolymer Foams

Sample	Density (g/cc)	Volume Fraction of Voids (%)
PMDA/3FDA/PI (control)	1.34	-
1	1.09	18.7
2	1.16	13.4
3	1.10	17.9
4	1.11	17.0
5	1.17	12.3

homogenous than expected. For example, the pore sizes were observed to range from 50 -100 Å for copolymers 1 to 3, and 500-800 Å for copolymers 4 and 5. Magnification of one of the pores of the 8000 g/mole copolymer, suggested that regions of the polyimide containing the PO grafts may have agglomerated into larger domains, which upon foaming provided larger voids. These results led to the study of the effect of varying composition on the size and shape of the pores arising from higher molecular weight poly(propylene oxide), i.e., PO graft length of 8000 g/mole. Copolymers of four different poly(propylene oxide) compositions, ranging from 7.5, 10, 15 and 25 wt.%, were synthesized and converted into nanofoams. As the PO composition varied from 7.5 to 25 wt%, TEM of the corresponding foams revealed that the morphology of the pore changed from an oval / spherically shaped discrete structure to a large agglomerated structure, resulting in bigger pores. The transformation from discrete to agglomerated type pores was observed to occur between 10 and 15 wt.% of PO, as shown in Figures 4.3.2.11 and 4.3.2.12.

The cellular structure of the foams was also confirmed using SAXS. The SAXS profile for the unfoamed copolymers 1 and 3, as well as for the corresponding foamed polyimide films exhibited a well defined peak . The plot of intensity as a function of the scattering vector for copolymers 1 and 3 are shown in Figure 4.3.2.13 a and b. However, a similar peak was absent, as expected, for the PMDA/3FDA homopolymer (Figure 4.3.2.13 c). The presence of the sharp peak in the unfoamed film also proves the presence a phase separated morphology, as observed using DMTA, and that the dispersed poly(propylene oxide) phase has some ordering in the polyimide matrix. On foaming, the intensity of the SAXS peak greatly increased, strongly supporting micro pore formation in the polyimide matrix. Specifically, the generation of pores would greatly increase the scattering contrast relative to that before the degradation of the poly(propylene oxide). The fact that the peak position has remained nearly constant in an angular position

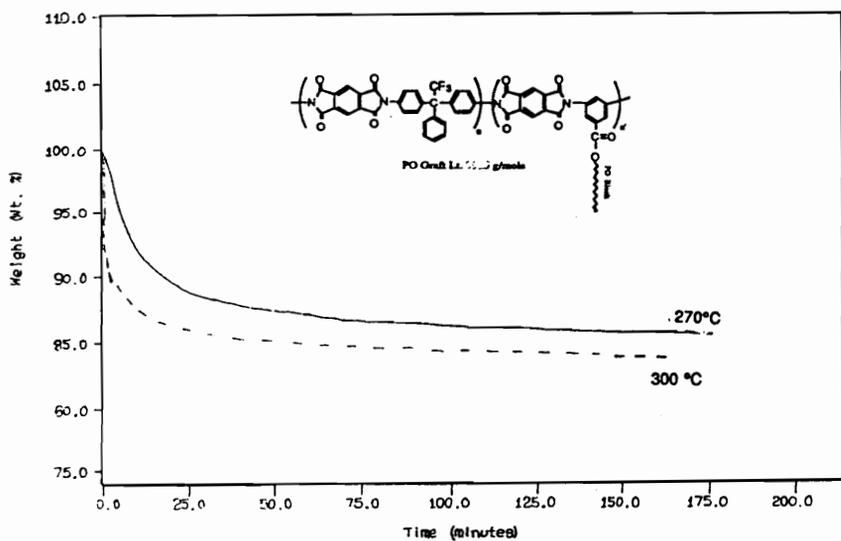
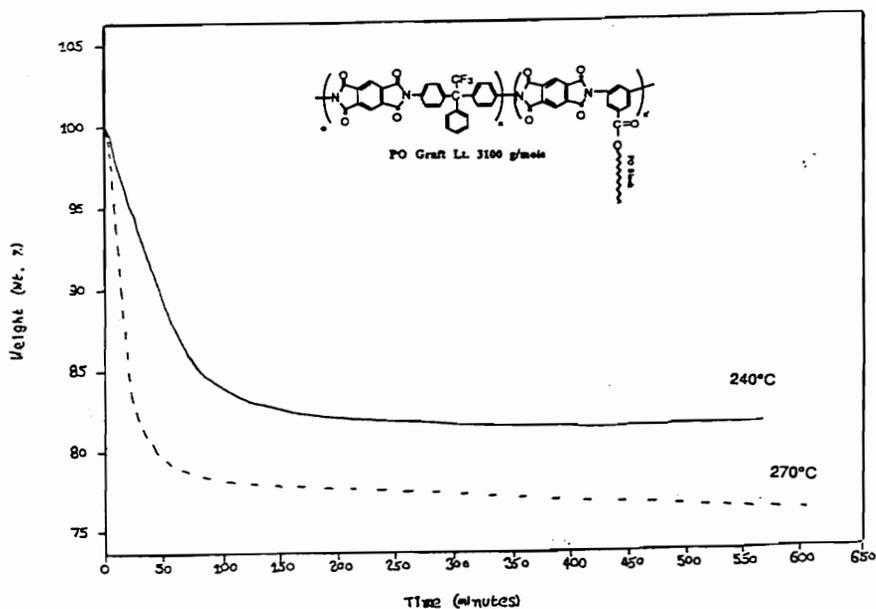


Figure 4.3.2.7 and 4.3.2.8 Isothermal TGA thermograms for Copolymers 1 at 240 and 270°C and for 4 at 270 and 300°C, respectively, in air (Heating rate 10°C/min)

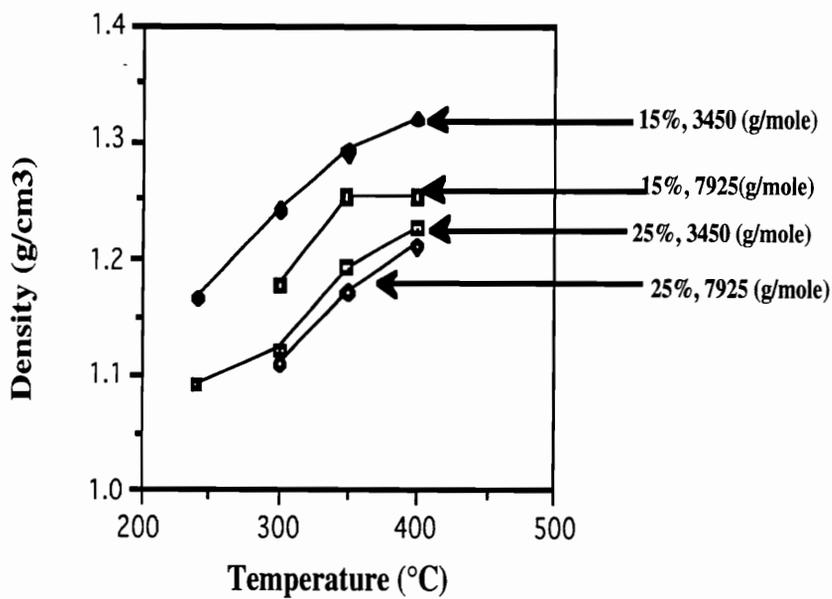


Figure 4.3.2.9 Thermal Stability of Polyimide Nanofoams (Plot of room temperature (25°C) density as a function of aging temperature)

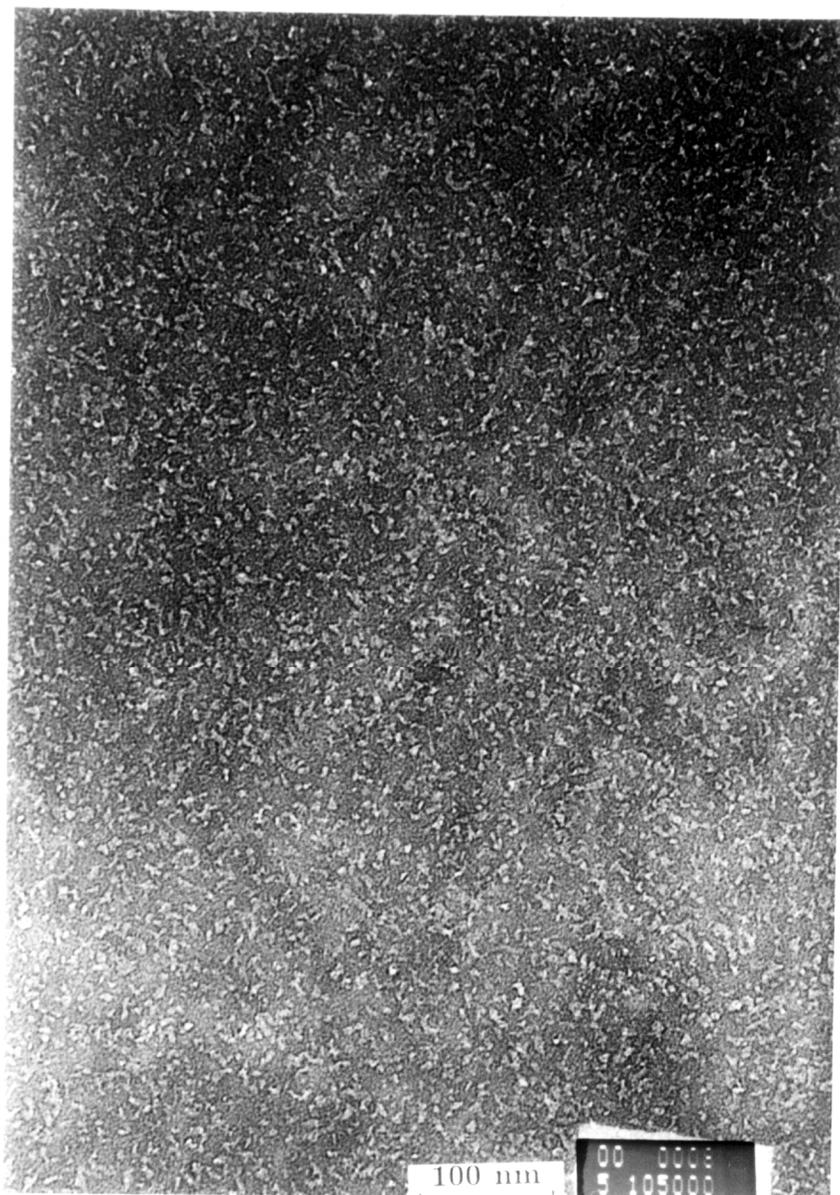
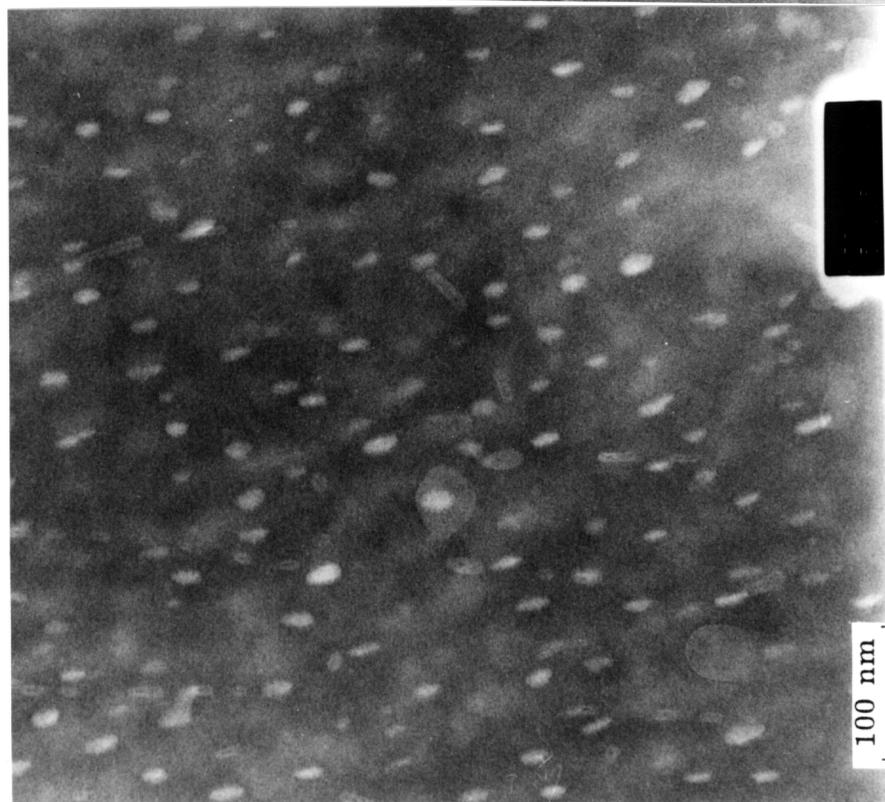


Figure 4.3.2.10 Electron Micrograph of Polyimide Nanofoams Derived from Graft Copolymer 4 (187,000 X)

7.5 wt. % poly(propylene oxide)



10 wt. % poly(propylene oxide)

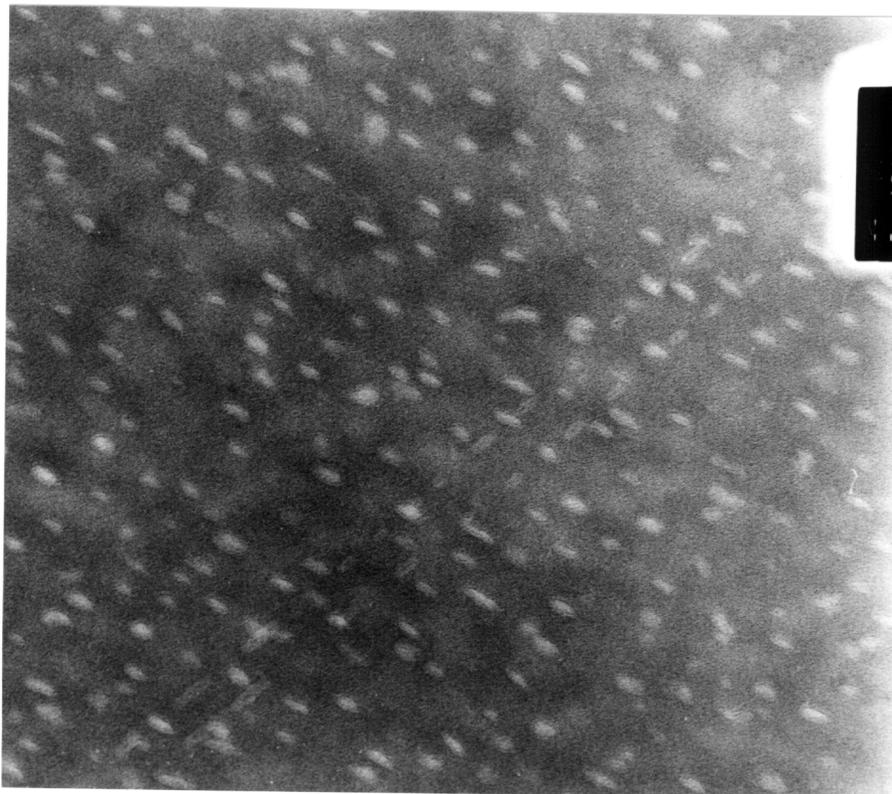
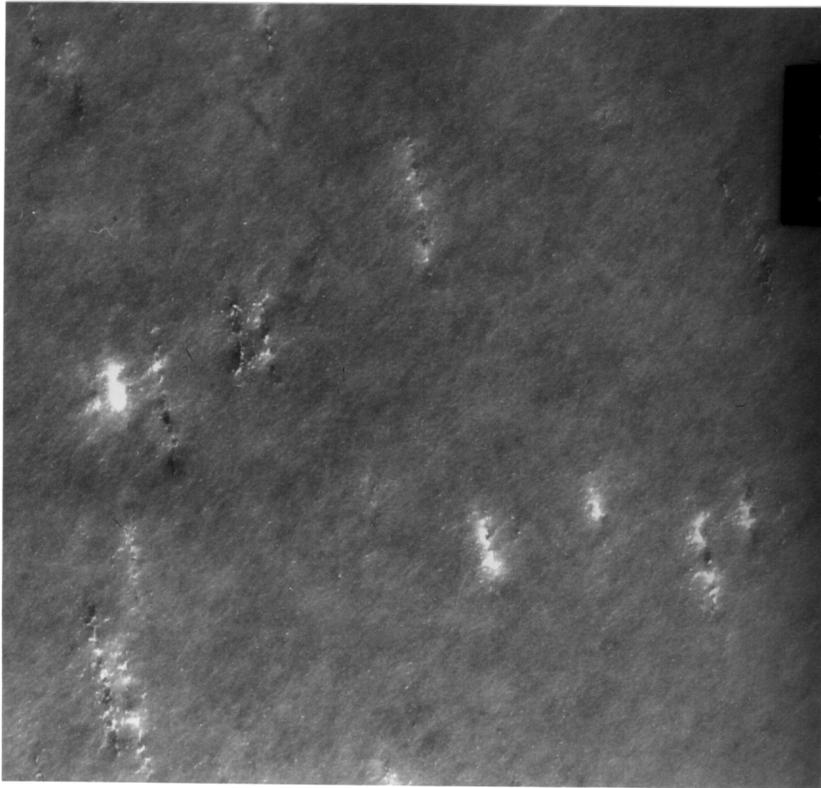


Figure 4.3.2.11 Electron Micrograph Showing the Effect of Chemical Composition of Poly(propylene oxide) Mol.wt. 8000 g/mole on the Foam Structure (187, 000 X)

15 wt. % poly(propylene oxide)



25 wt. % poly(propylene oxide)

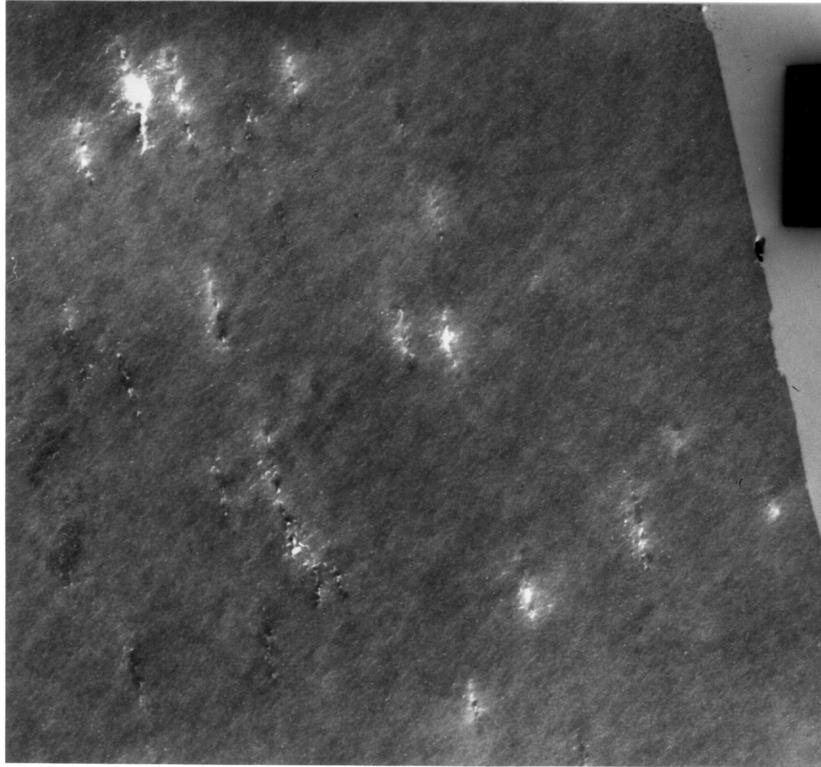


Figure 4.3.2.12 Electron Micrograph Showing the Effect of Chemical Composition of Poly(propylene oxide) Mol.wt. 8000 g/mole on the Foam Structure (187, 000 X)

also strongly indicates that the general pore structure is similar in nature to that prior to poly(propylene oxide) degradation. The estimated "d" spacing, which relates to the distance between the pores, has been obtained from the slit smeared data as 28 nm. Unfortunately, such well defined peaks were not observed for both foamed and the unfoamed copolymers 4 and 5. DMTA shows the presence of two T_g 's: a low temperature transition corresponding to the poly(propylene oxide) phase, and a high temperature transition corresponding to the polyimide phase, which supports the microphase separated morphologies. However, a SAXS peak of the unfoamed films of copolymer 4 and 5 was not observed. Also on foaming, though the density of the foams generated from copolymers 4 and 5 showed a drop in density, no peak was observed in SAXS. Based on TEM results, it is suggested that the size of the pores obtained from copolymers 4 and 5 were large enough, that the peak had moved to very small angles, which prevented their detection by SAXS.

Thus, polyimide nanofoams were prepared using both the block and graft copolymer approach for fully cyclized polyimide and poly(propylene oxide) systems. It should be again noted that in the case of the block copolymers, the volume fraction of the voids do not quantitatively correspond to the volume fraction of the propylene oxide, as in the initial copolymer. For both the block and graft copolymers, at lower poly(propylene oxide) compositions, this discrepancy, though present, seems to be smaller than for the higher poly(propylene oxide) compositions. This is probably due to the fact that the degradation products of the poly(propylene oxide) phase plasticize the imide matrix, which can reduce the apparent T_g of the imide phase so that it approaches the experimental foaming temperature. Thus, substantial mobility of the imide matrix can occur, which results in the partial collapse of the foam. In order to address this issue, the solubility parameter of the PMDA/3FDA polyimide was experimentally obtained using intrinsic viscosity measurements of the homopolyimide in different solvents.¹⁸¹ This was later verified by

swelling measurements of the crosslinked PMDA/ 3FDA polyimide oligomers in different solvents.²⁰⁶

Solubility parameter values by intrinsic viscosity measurement, are based on the fact that the intrinsic viscosity of a polymer is related to the size of the polymer chain in solution. If the polymer is dissolved in a thermodynamically better solvent, the polymer molecules are expanded and their apparent molecular size should be larger. The reverse would be expected to occur when the polymer is dissolved in a poor solvent. Thus if the solubility parameter of the solvent is equal to that of the polymer, the intrinsic viscosity of the polymer in the solvent should show a maximum. By selecting solvents with known solubility parameters, and measuring the intrinsic viscosity of the polymer in these solvents, the solubility parameter of the polymer can be estimated. Table 4.3.2.4 lists the solubility parameters of the solvents used, and Figure 4.3.2.14 shows the plot of intrinsic viscosity of a PMDA/3FDA homopolyimide measured at room temperature in different solvents against the solubility parameter of the corresponding solvents. The maximum intrinsic viscosity was approximately $11.0 (\text{cal} / \text{cm}^3)^{1/2}$. Thus, this value was used for the PMDA/3FDA polyimide.

The solubility parameter of the PMDA/3FDA polyimide was verified by using the solvent uptake experiment of a crosslinked polymer. In order to accomplish this, a soluble PMDA/3FDA based poly(amic alkyl ester) oligomer of 3000 g/mole molecular weight endcapped with 3-ethynyl aniline was synthesized. A two-step synthetic procedure was used to synthesize the ethynyl endcapped oligomer. In the initial step, 3FDA and 3-ethynyl aniline were charged into a three-necked flask to which N-methyl pyrrolidone and pyridine was added. To this solution, the meta-diester diacyl chloride of pyromellitic dianhydride was added, and stirred under nitrogen for 12 hours to afford the poly(amic alkyl ester) solution. The resulting polymer was precipitated in a water-methanol mixture and dried in

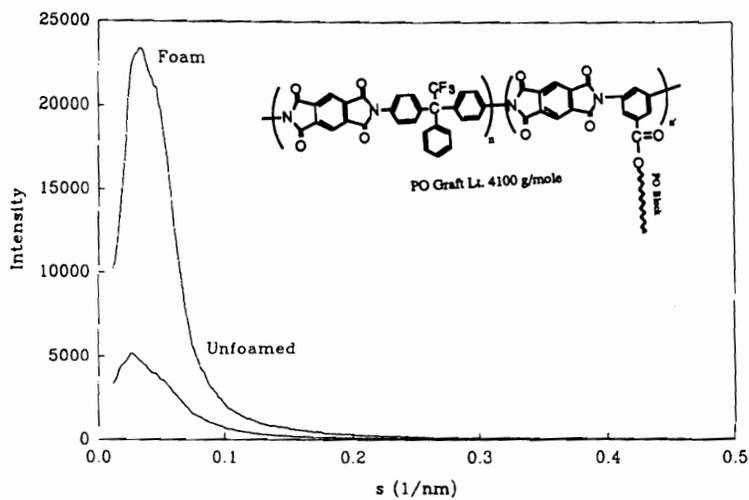
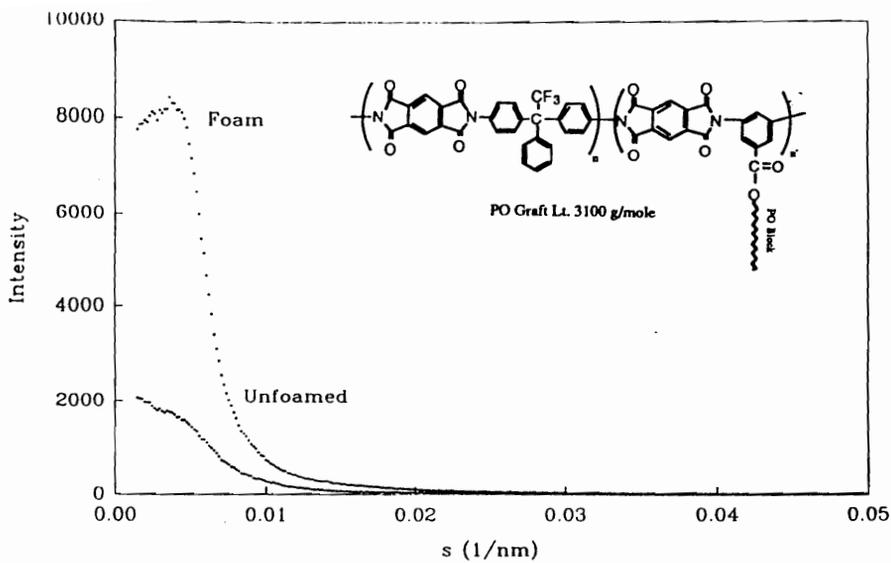


Figure 4.3.2.13 SAXS Plot of Intensity as a Function of the Scattering Vector for Copolymer 1 and 3 (Figure a and b respectively).

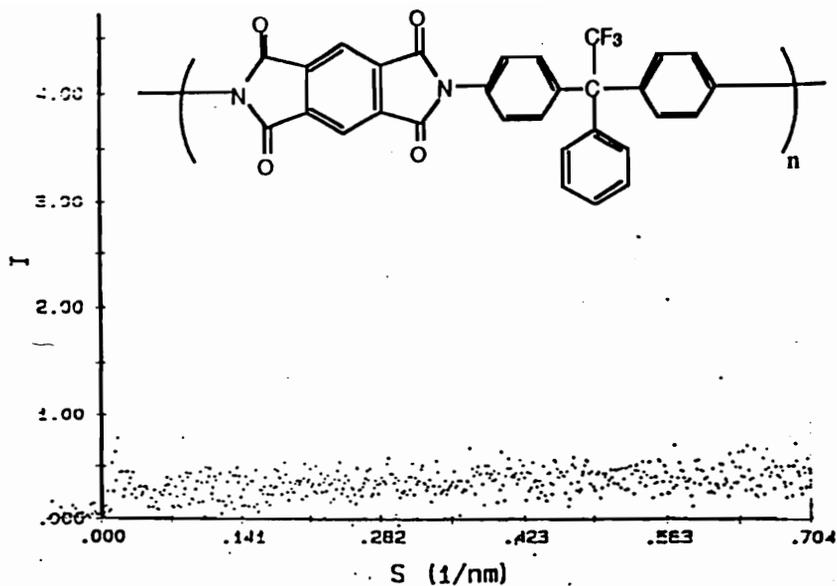


Figure 4.3.2.13c SAXS Pattern for PMDA/3FDA Homopolyimide.

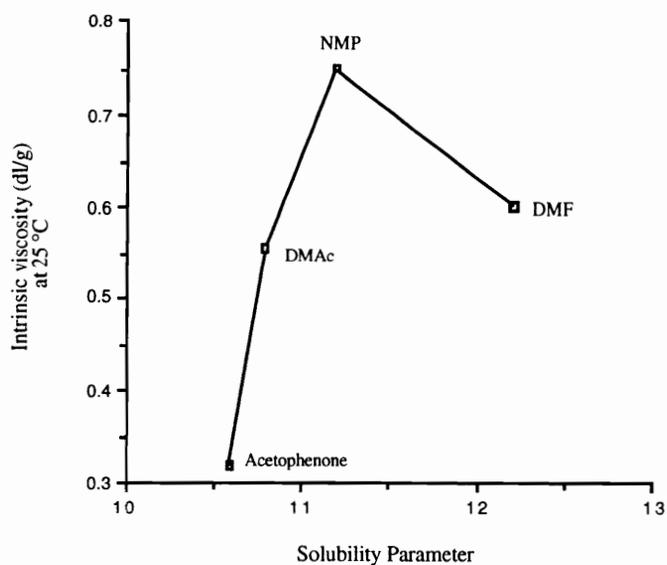


Figure 4.3.2.14 The Plot of Room Temperature Intrinsic Viscosity of PMDA/3FDA Homopolyimide Against the Solubility Parameter $(\text{cal} / \text{cm}^3)^{1/2}$ of the Corresponding Solvents

a vacuum oven at 100°C for 12 hours. The molecular weight of the polyimide was confirmed by end group analysis using ^1H NMR. The ethynyl endcapped polymer was later dissolved in NMP, cast on to a glass plate, and cured under nitrogen for 3 hours at 300°C. The resulting crosslinked polyimide film was cut into small pieces and added to several different solvents in order to perform the equilibrium swelling measurements. These results are provided in Figure 4.3.2.15. Based on this experiment, the solubility parameter was estimated to be $11.1 (\text{cal/cc})^{1/2}$.

Having established the solubility parameter of the homopolyimide, and in order to compare this value with the solubility parameter of the byproducts obtained from the degradation of the PO phase, Thermogravimetric/Gas Chromatography/Mass Spectroscopy (TGA/GC/MS) analysis was performed on copolymer 4 under a helium atmosphere to obtain all the degradative products arising from the PO degradation. The TGA/GC/MS technique allows one to analyze the volatiles evolved from a sample during a thermogravimetric (TGA) experiment. In this technique, the purge gas helium was swept over the sample in the TGA experiment. The evolved volatiles from the sample were carried by the purge gas through the heated transfer line to the mass spectrometer. During the thermogravimetric / mass spectroscopy (TGA/MS) experiment, a portion of the evolved volatiles were cryogenically trapped on a GC column. After TGA/MS analysis, the trap was heated and gas chromatography / mass spectroscopy (GC/MS) analysis was performed on the trapped volatiles. This experiment provided clear insight on the volatiles evolved due to PO degradation. Seven major degradative byproducts were observed and these are listed in Table 4.3.2.5 , along with their respective solubility products.

The solubility parameter were obtained for the byproducts from the Hand Book of Polymer Science. Acetaldehyde, acetone, carbon dioxide and water were observed to comprise nearly 80% of the byproducts from poly(propylene oxide) degradation. Thus, it was observed that the solubility parameter of the PMDA/3FDA homopolyimide was in

Table 4.3.2.4 List of Intrinsic Viscosity of PMDA/3FDA/PI in Different Solvents and the Respective Solvents Solubility Parameters

Solvent	Intrinsic viscosity(dl/g) at 25°C	d (cal/cm ³) ^{1/2}
Acetophenone	0.32	10.6
DMAc	0.557	10.8
NMP	0.749	11.2
DMF	0.602	12.2
DMSO	0.341	12.0

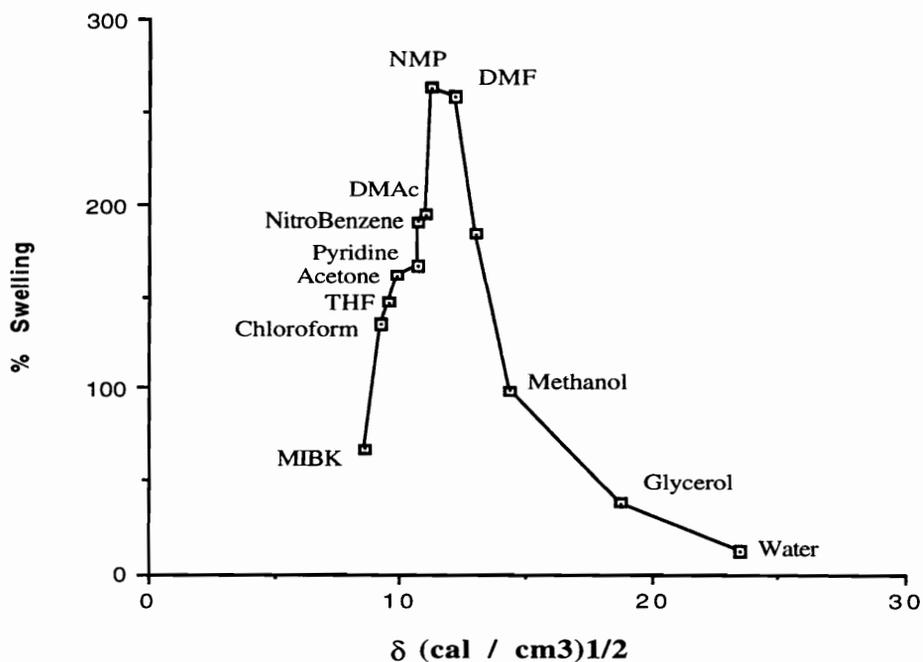


Figure 4.3.2.15 Solubility Parameter Calculation of PMDA/3FDA Polyimide using Swelling Experiments

Table 4.3.2.5 Solubility Parameter of the Major Degradative Products Obtained on Degradation of PMDA/3FDA/PO (25%, 8000g/mole) Graft Copolymer

Degradative byproducts	$d_{calc} (Cal/cm^3)^{1/2}$
PMDA/3FDA/PI (control)	10.4
PO	8.9
Carbondioxide	7.4
Water	23.4
Acetone	9.9
Acetaldehyde	10.3
diisopropylether	6.9
isopropylacetate	4.4
cyclic ethers	4.2

close proximity to the degradative byproducts of poly(propylene oxide), primarily acetone and acetaldehyde. Hence some plasticization of the PMDA/3FDA polyimide matrix by acetone and acetaldehyde during the degradation of poly(propylene oxide) was possible and resulted in partial collapse of the foam. This could explain the lower amount of voids, in comparison to the poly(propylene oxide) volume fraction in the copolymer.

The second problem associated with polyimide foams obtained from completely cyclized PMDA/3FDA polyimides is the inability to spin cast thin films of both homo and copolymeric materials. These materials proved satisfactory for the generation of thicker films (> 1 mil) for density, SAXS and TEM measurements. However, difficulties were experienced trying to spin cast NMP solutions of the polymers on to the silicon substrate. The thin films samples were observed to dewet, resulting in the polyimide to “puddling up” towards the center, thus forming non uniform films. Changes in processing temperature, spin rate, and concentration of the solution or solvent were unsuccessful in alleviating this problem. This hampered further characterization on the foamed films, such as thin film stress and refractive index measurements. To address the issue of developing more soluble spin coatable materials graft copolymers of poly(amic alkyl ester) were developed and this is discussed in the next section.

4.3.3. Synthesis and characterization of polyimide foams from PMDA/3FDA based poly(amic alkyl ester)-poly(propylene oxide) graft copolymers

The poly(amic alkyl ester)s approach was investigated to improve the processability of polyimide systems. The derivatization of the carboxylic acid moieties along the poly(amic acid) backbone in the form of alkylester groups, provides increased synthetic flexibility since they are soluble in a variety of solvents and solvent mixtures. They also provide a solution to hydrolytic instability associated with the traditional poly(amic acid) precursor. Through the judicious choice of the alkyl moiety, considerable flexibility is afforded in the imidization temperature. The effect of alkyl groups on imidization temperature has been very well characterized by Volksen et al. for the PMDA/ ODA system.⁸² For instance, poly(amic alkyl ester)s which employs the t-butyl ester group, imidizes at temperatures comparable to those of the poly(amic acid) analog, while those derived from ethyl or propyl derivatives imidize at substantially higher temperatures. These results are summarized in the Table 4.3.3.1.

The poly(amic alkyl ester)s are known to be more soluble in polar aprotic solvents in comparison to the corresponding polyimides which makes it desirable for high solid content formulations with significantly improved planarization characteristics, which are highly desirable for electronics industries. Hence poly(amic alkyl ester)s are a very versatile polyimide precursors for improved dielectric coatings.

The use of poly(amic alkyl ester) copolymers as a route toward polyimide foams introduces imidization as an additional parameter to be considered, in addition to the other parameters such as solvent removal, foaming temperature etc. In order to develop stable foams using the poly(amic alkyl ester) approach, both imidization and solvent removal must occur at temperatures below the decomposition temperature of the labile block to

Table 4.3.3.1 Effect of Alkyl Group on the Imidization Characteristics of PMDA/ODA
Poly(amic alkyl ester)s ⁸²

Poly(amic alkyl ester)	Maximum Imidization Temperature	Imidization Temperature Regime
	(°C)	(°C)
t-Butyl	193	170-210
Ethylglycolyl	217	190-350
Propargyl	224	200-300
Ethyl	255	240-350
Isopropyl	269	240-290

afford the polymer matrix in the high T_g imide form. The extent of imidization is expected to depend on the choice of the alkyl group in the amic ester synthesis, i.e., the structure of the base poly(amic alkyl ester). The imidization temperature is also thought to depend on the choice of the diacyl diacid chloride isomer of PMDA (meta or para) used in the synthesis of the polymer, and to some extent on the diamine of choice. In the case of the poly(propylene oxide) copolymers, the maximum imidization temperature is defined by the degradation temperature of the poly(propylene oxide).

Based on previous results obtained from the PMDA/ODA system by Volksen et al., it was determined that the ethyl ester would be the best choice due to the ease of synthesis and its ability to provide superior thin film coatings. The use of ethyl ester instead of isopropyl or t-butyl ester was also expected to minimize polymer shrinkage due to the small size of the alkyl group. Having decided on the ethyl ester, to study the effect of isomer structure and 3FDA on the imidization temperature range, controlled molecular weight PMDA/3FDA based poly(amic alkyl ester)s, from both meta and para isomers of PMDA diester diacidchloride, were prepared and characterized.

Poly(amic alkyl ester)s of PMDA/3FDA endcapped with t-butyl phthalic anhydride were synthesized and this reaction scheme is provided in Figures 4.3.3.1 and 4.3.3.2. In order to eliminate the effects of molecular weight on imidization temperature, the molecular weights of both the meta and para poly(amic alkyl ester)s were controlled to 15000 g/mole. The synthesis involved the incremental addition of diethyl ester diacyl chloride of PMDA (meta or para isomer), dissolved in dry THF, to a solution of mono functional endcapper t-butyl phthalic anhydride and 3FDA in NMP containing pyridine as the acid acceptor. The solid composition was maintained at 15% for each of the polymerization's. The solution was stirred under nitrogen for 12 hours, after which the polymers were isolated in the methanol/water mixture, rinsed with water and methanol, and vacuum dried at 50°C. The

molecular weight of the polymer was obtained by integrating the methyl protons on the t-butyl phthalic anhydride with the aromatic protons or the methyl protons of PMDA alkyl ester, as demonstrated in Figure 4.3.3.3 and furthermore, Table 4.3.3.1, shows that good molecular weight was achieved for both isomeric polymers. Intrinsic viscosity measurements of these poly (amic alkyl esters) were obtained in NMP and these results are also reported in Table 4.3.3.1.

Table 4.3.3.1 Characteristics of t-butyl Terminated Isomeric Poly(amic alkyl ester)

Poly(amic alkyl ester) Isomer Structure	Molecular Weight (g/mole)		Intrinsic Viscosity (dl/g), NMP, 25°C
	Target	From ¹ H NMR	
PARA ISOMER	15,000	13,300	0.34
META ISOMER	15,000	12,600	0.29

In order to study the effect of isomeric PMDA structures on the imidization behavior of PMDA/3FDA based poly(amic alkyl ester), DSC, TGA and dynamic mechanical analysis were performed on the t-butyl endcapped polymers. Differential Scanning Calorimetric (DSC) study of the above t-butyl terminated poly(amic alkyl ester)s was performed under nitrogen atmosphere, beginning at room temperature and raising to 450°C, at a scan rate of 10°C/min. Both the polymers exhibited a broad endotherm corresponding to the conversion of the poly(amic alkyl ester) to the polyimide. The imidization temperature was observed to range from 180 to 380°C for the para isomer, and from 205 to 385°C for the meta isomer. These temperatures were observed to be a little

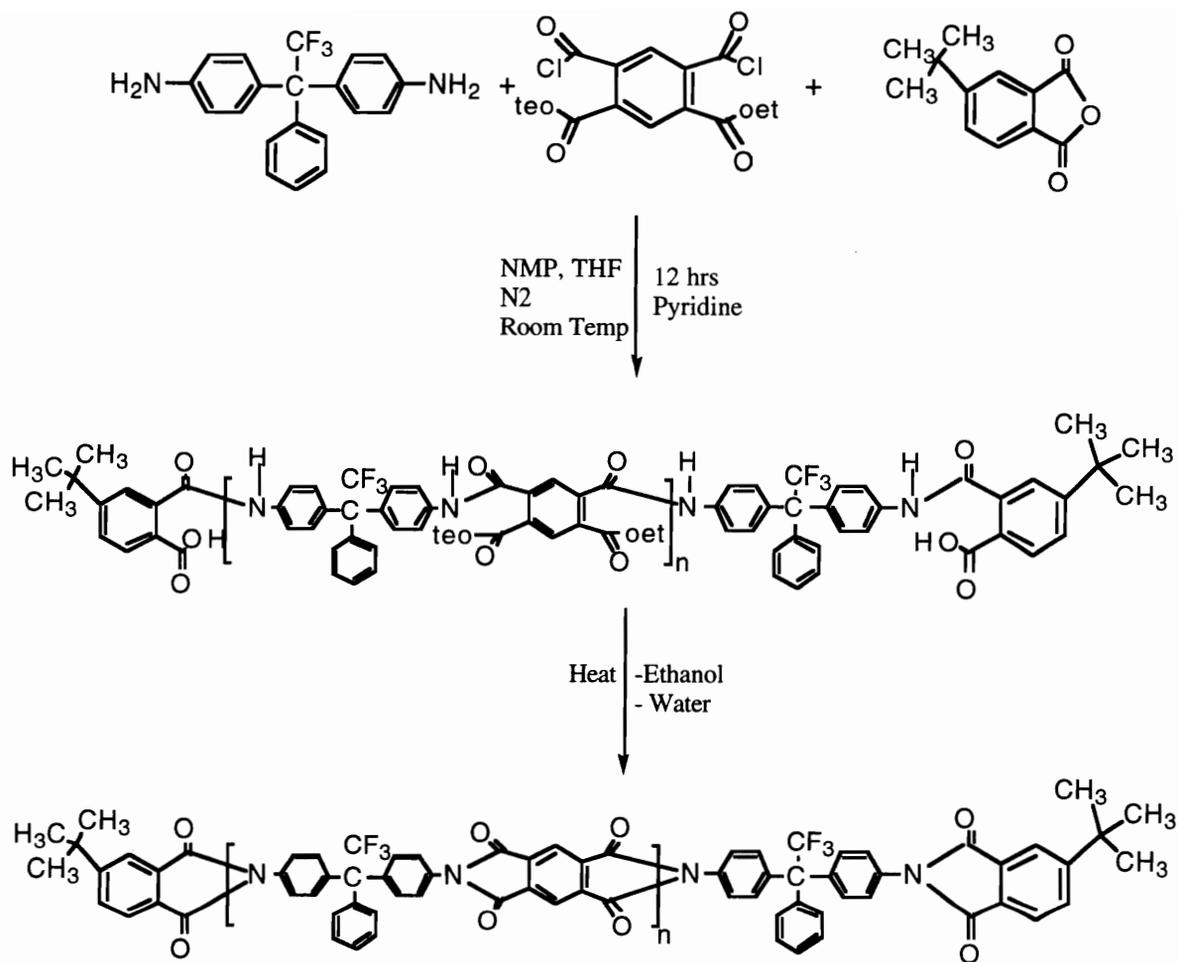


Figure 4.3.3.1 Synthesis of t-butyl Endcapped PMDA/3FDA meta-Poly(amic alkyl ester)

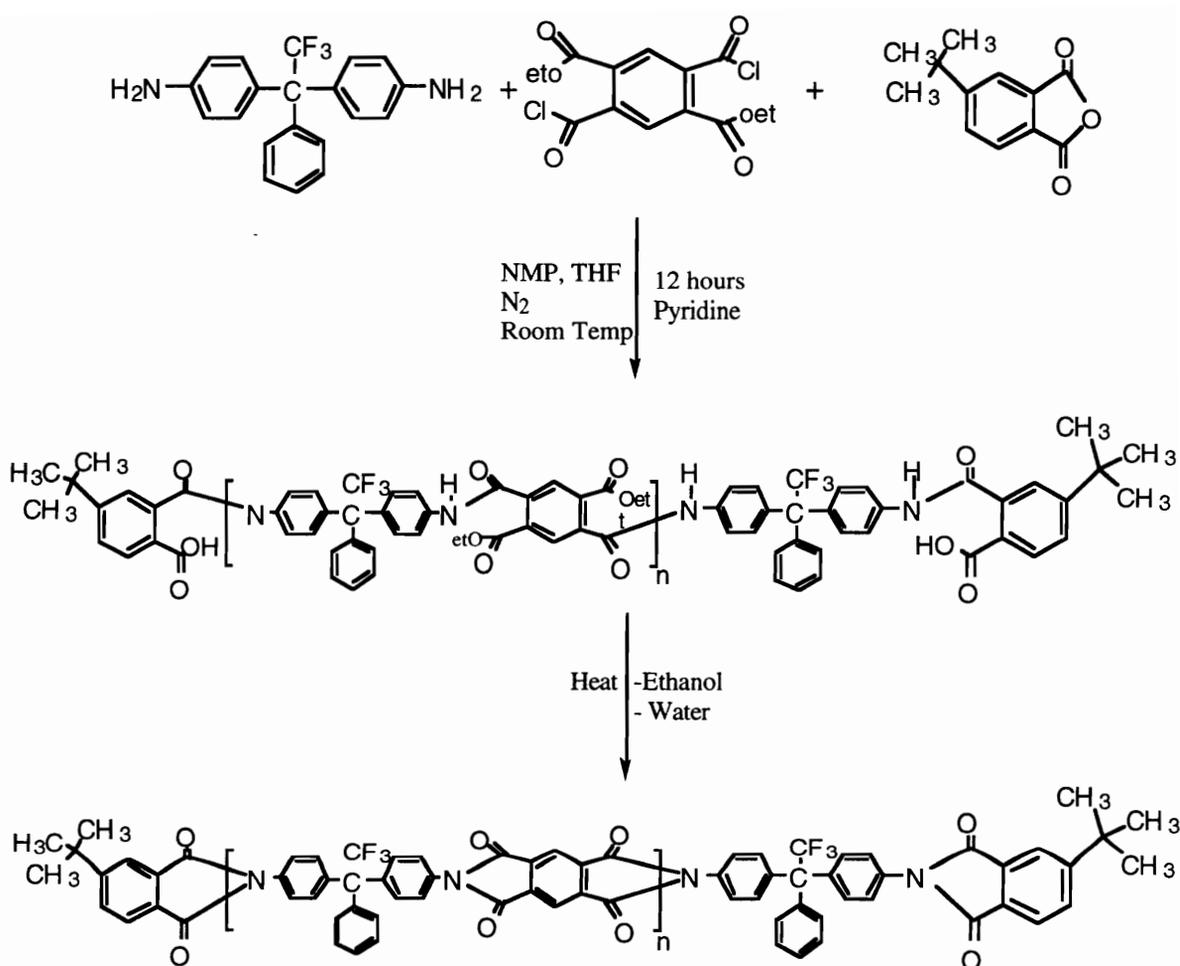


Figure 4.3.3.2 Synthesis of t-butyl Endcapped PMDA/3FDA para-Poly(amic alkyl ester)

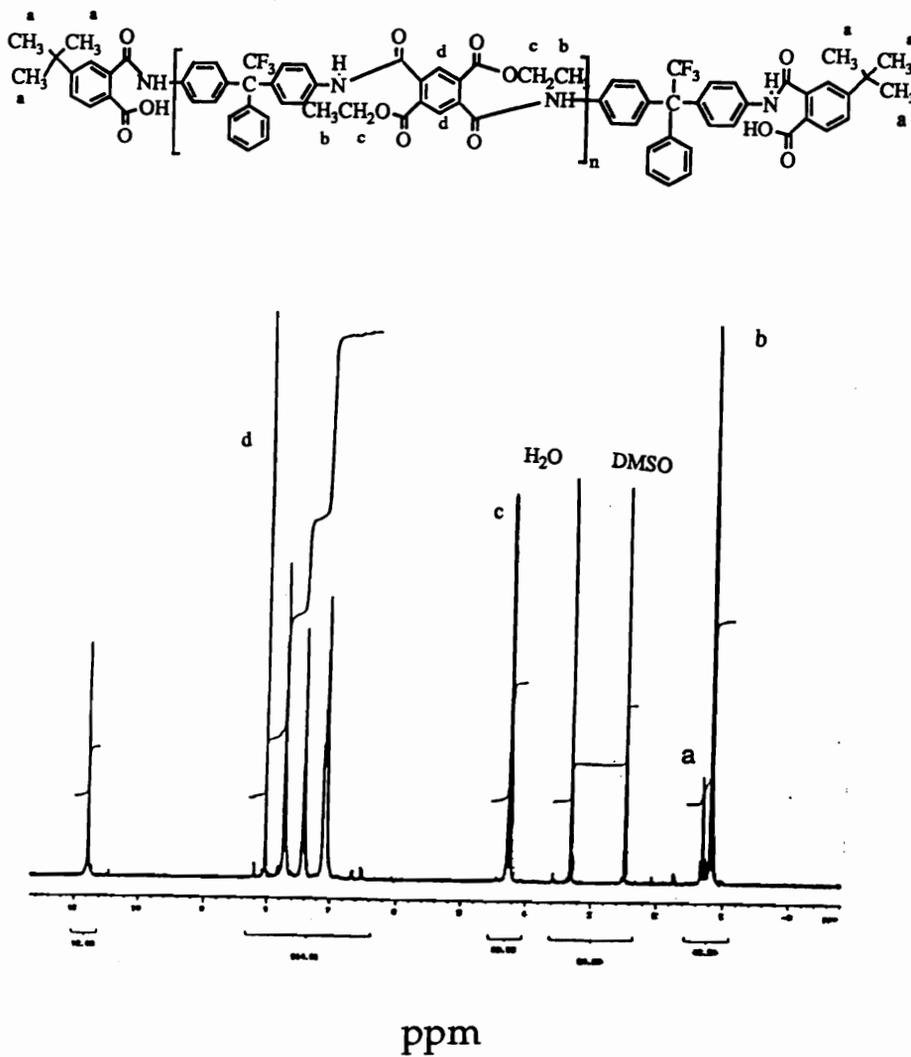


Figure 4.3.3.3 a) ¹H NMR Spectrum of t-butyl Endcapped PMDA/3FDA Poly(amic alkyl ester) for the Para isomer, b) for the Meta isomer

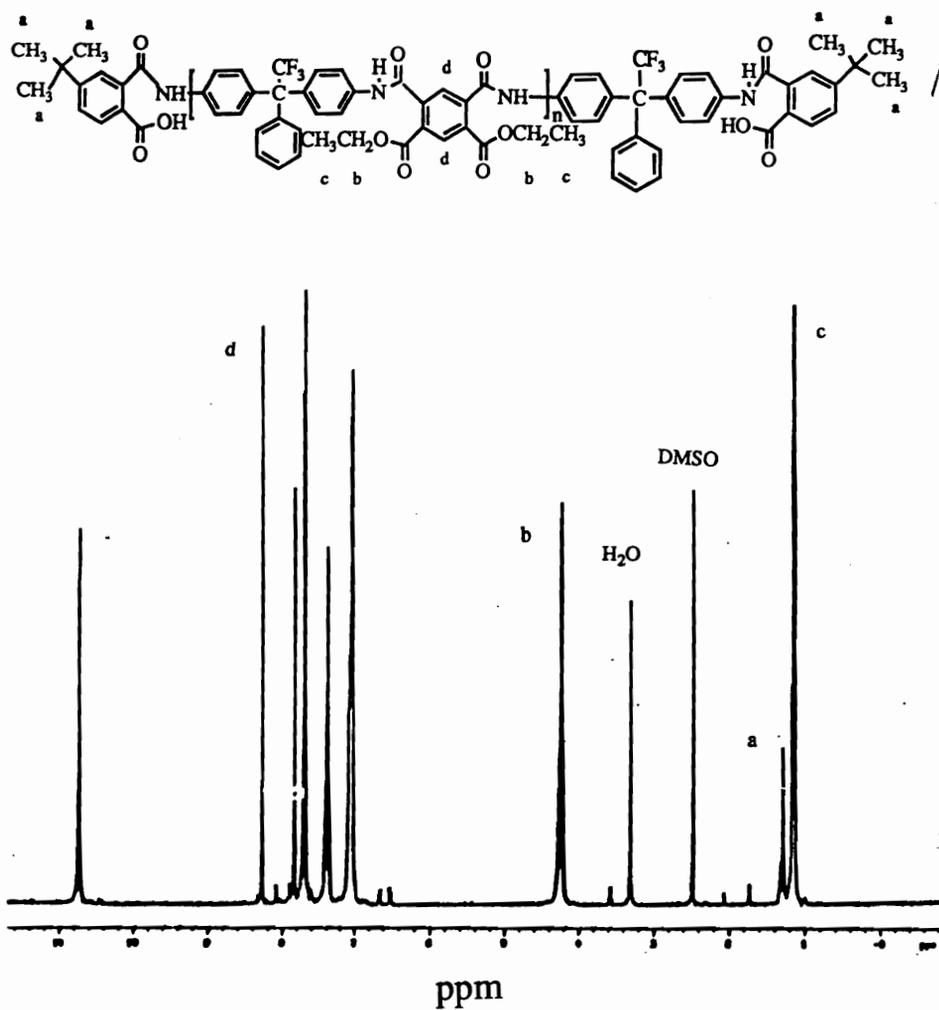


Figure 4.3.3.3 b) ¹H NMR Spectrum of t-butyl Endcapped PMDA/3FDA Poly(amic alkyl ester) for the Meta isomer

higher than that observed for the PMDA/ODA system. The maximum imidization temperatures for the para isomer was 282°C, while that for the meta isomer was 290°C. Similar results were also observed in the case of TGA experiments. The TGA of the poly(amic alkyl ester) exhibited a two-step degradation profile as expected. The first step occurring at 180 to 225°C for both the materials, corresponds to the loss of ethanol and the formation of the imide ring. The second step, occurring at beyond 500°C, corresponds to the degradation of the polyimide. In the case of the para isomer, the imidization reaction ranged from 195 to 395°C, while that for the meta isomer was observed to range from 211 to 393°C. The maximum imidization temperature was interpreted as the peak of the TGA derivative curve, which was observed to be 279°C for the para isomer and 290°C for the meta isomer. These results are provided in Table 4.3.3.2. The DSC and the TGA profiles for both the isomers are provided in Figure 4.3.3.4 and 4.3.3.5, respectively.

Dynamic mechanical analysis was also used to follow the imidization reaction of the poly(amic alkyl ester)s to the polyimide structures. On conversion of the poly(amic alkyl ester) to the polyimide the chains are expected to become stiffer and, hence, the modulus of the polyimide is expected to be higher than the corresponding poly(amic alkyl ester). Thus, by following the increase in the modulus of the sample was be possible to obtain the range at which the imidization reaction was occurring. In order to study the effect of poly(amic alkyl ester) isomer on the imidization temperature, the polymers were dissolved in tetrahydrofuran and coated on to a glass braid. The samples were dried in air, then in a vacuum oven for more than 48 hours. DMA measurements were performed on the braid-coated samples in air 30 to 450°C at a rate of 5°C /min. The storage modulus of the samples was observed to increase from around 195°C for the para isomer, indicating the onset of the imidization. The modulus was observed to increase up to 405°C, indicating almost complete imdization However, in the case of the meta isomer, the modulus was observed to initially drop at around 100°C indicating the softening of the polymer, followed

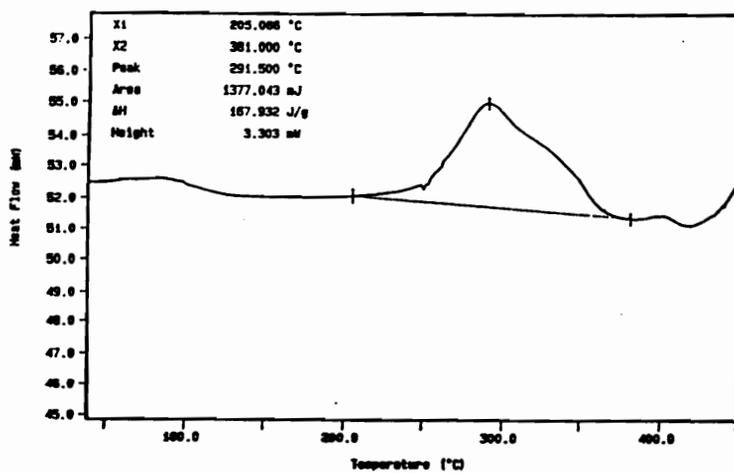
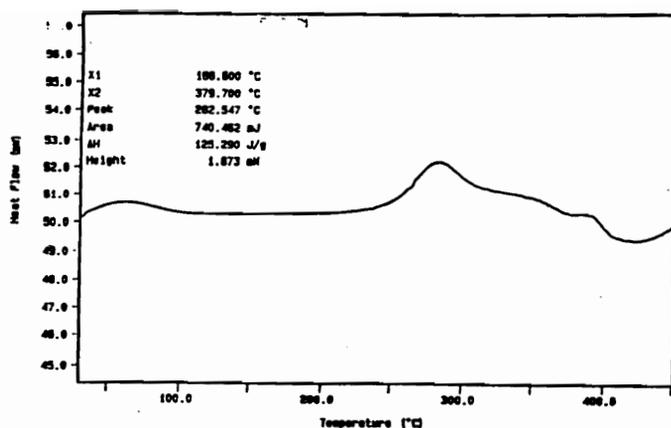


Figure 4.3.3.4 Differential Scanning Calorimetric Analysis of Isomeric t-butyl Endcapped Poly(amic alkyl ester). a) spectra of the para isomer, b) spectra of the meta isomer.

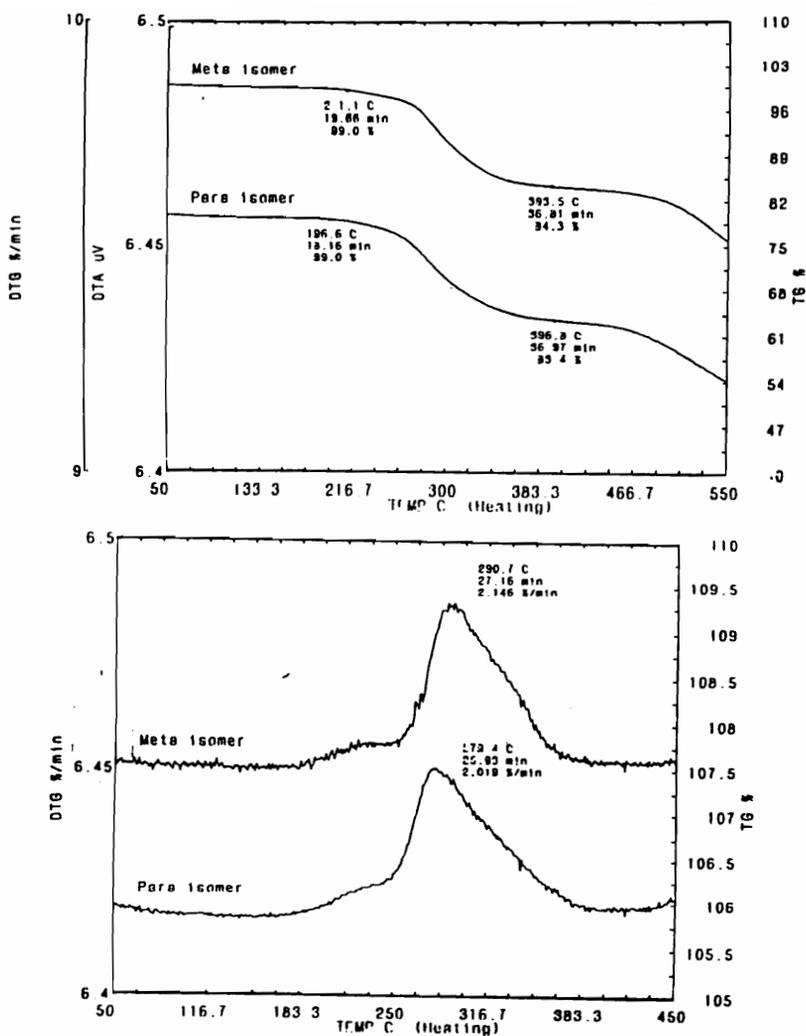


Figure 4.3.3.5 Thermogravimetric Analysis of Isomeric t-butyl Endcapped Poly(amic alkyl ester). a) TGA Thermograms of the para and meta Isomer, b) TGA Derivative Curve for para and meta Isomer.

by an modulus increase occurring at around 208°C. The imidization reaction resulting in the increase in the modulus was observed to occur up to 373°C. These results are provided in Table 4.3.3.2. The dynamic mechanical spectrums of the para and meta poly(amic alkyl ester) are provided in Figure 4.3.3.6.

Table 4.3.3.2 Thermal Characteristics of the t- butyl Endcapped PMDA/3FDA Poly(amic alkyl ester)

Poly(amic alkyl ester) isomer	Imidization Temperature (°C)				
	By DSC		By TGA		By DMA
	Range	Maximum	Range	Maximum	Range
Para	180 - 380	282	195 - 395	279	195 - 405
Meta	205 - 385	291	211 - 393	290	208 - 373

Thus, after analyzing the base poly(amic alkyl ester)s, it was determined that the meta- poly(amic alkyl ester) of PMDA/3FDA was preferred over the para isomer, as it was much more soluble and had a softening temperature much lower than the polymer obtained from the para isomer. The higher solubility of the meta poly(amic alkyl ester) makes it possible to prepare very high concentration polymeric solutions for use in spin coating. It was observed that the poly(amic alkyl ester) obtained from the meta isomer provided better thin film coatings on silicon wafer, when compared to the para isomer. In attempting film formation from the polymer obtained from the para isomer, thin films were observed to crack while no such cracking was observed for the films obtained from the meta isomer.

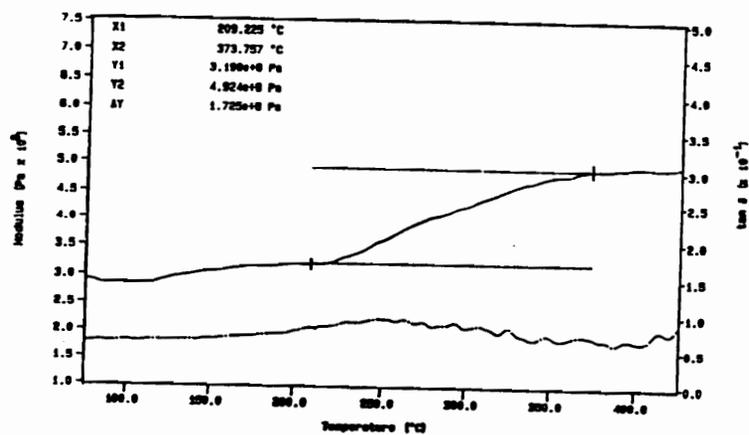
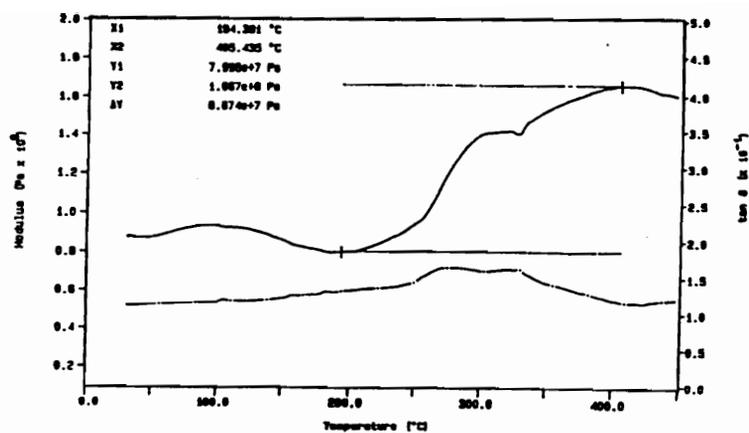


Figure 4.3.3.6 Dynamic Mechanical Analysis of Isomeric t-butyl Endcapped Poly(amic alkyl ester). a) spectra of the para isomer, b) spectra of the meta isomer. (Heating rate = 5°C), Frequency = 1 Hz)

Thus the next step was to prepare poly(amic alkyl ester) copolymers for the development of polyimide foams.

The procedure for the synthesis of the PMDA/3FDA poly(amic alkyl ester) graft copolymers was analogous to that of t-butyl endcapped PMDA/3FDA poly(amic alkyl ester) . The graft copolymers were generated using diamino benzoate terminated poly(propylene oxide) macromonomers. First incremental amounts of the meta diacylchloride diethylester of PMDA were added to a NMP solution of diamine terminated poly(propylene oxide), 3FDA and pyridine. The solid composition for each of the polymerization's was maintained at approximately 15%. The polymerization was allowed to proceed for at least 12 hours. The copolymers were isolated in a methanol/water mixture, rinsed with water to remove remaining salts, stirred in isopropanol for 5 hours to remove possible poly(propylene oxide) homopolymers, and finally dried at 50°C for 24 hours under vacuum.

Only one poly(propylene oxide) block length was investigated (mol. wt 3100 g/mole) in compositions of 15 and 25 wt.%. The composition of poly(propylene oxide) in the copolymer was assessed by both ¹H NMR and TGA. Figure 4.3.3.7 shows the ¹H NMR of the poly(amic alkyl ester) copolymer containing 25 wt.% of the poly(propylene oxide) block. These results are provided in Table 4.3.3.3. Figure 4.3.3.8 shows the dynamic TGA profile of the imidized copolymer obtained from the meta-poly(amic alkyl ester) copolymer 1. The amount of propylene oxide incorporated into the copolymer was observed to be somewhat lower than calculated, probably due to extraction of the poly(propylene oxide) rich copolymers.

The use of the poly(amic alkyl ester) copolymers makes imidization an additional consideration in their processing. Imidization and solvent removal must both occur below the decomposition temperatures of the labile block to afford the

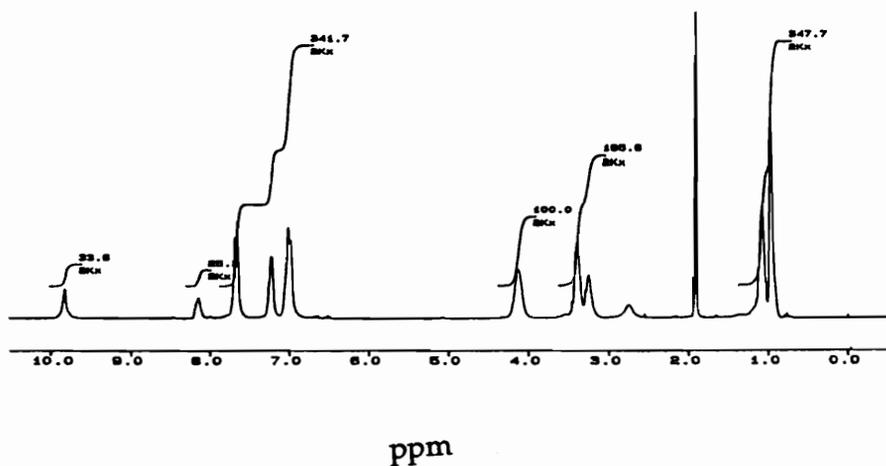
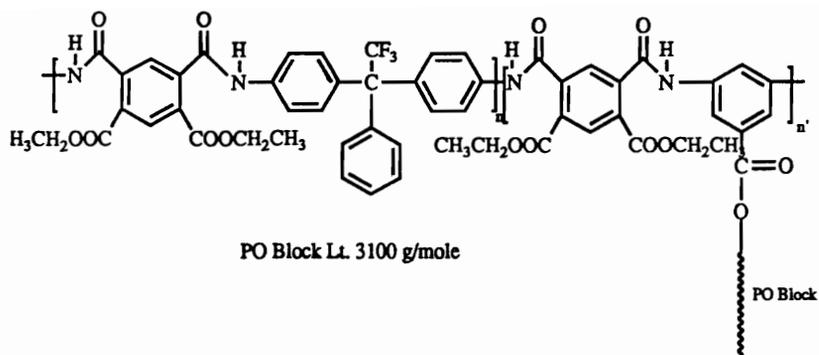


Figure 4.3.3.7 ^1H NMR of the Poly(amic alkyl ester) Copolymer Containing 25 wt.% of the Poly(propylene oxide) Block

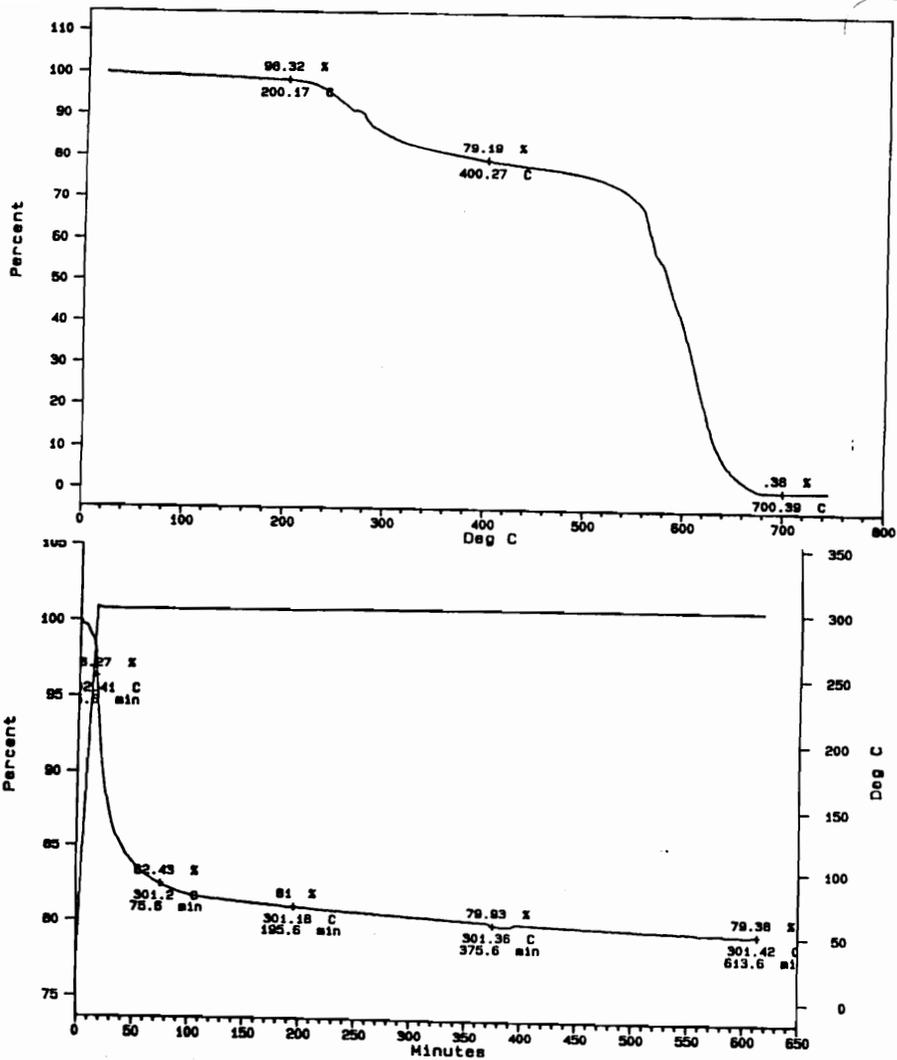


Figure 4.3.3.8 a) Dynamic TGA and b) Isothermal TGA of the Polyimide-Poly(propylene oxide) Copolymer Obtained from Imidization of Poly(amic alkyl ester) Copolymer Containing 25 wt.% of the Poly(propylene oxide) Block

Table 4.3.3.3 Characteristics of meta-poly(amic alkyl ester) of PMDA/3FDA

/Poly(propylene oxide) Copolymers. A as prepared sample and B obtained from Polyimide Film before Foaming

Sample	Poly(propylene oxide) mol. wt.	Target	Obtained From ¹ H NMR		From TGA
			A	B	
1	3100	25	19.8	15.7	19.0
2	3100	15	11.6	11	12.0

polymer matrix in high T_g imide form. In order to produce films from the alkyl ester copolymers, the samples were dissolved in NMP, cast on to a glass plate, and cured up to 300°C for 1 hour.

Dynamic mechanical results of the polyimide-poly(propylene oxide) graft copolymers obtained from poly(amic alkyl ester) copolymers were similar to those of originally prepared polyimide-poly(propylene oxide) copolymers. These materials also exhibited two transitions: a low temperature transition occurring at around -60°C corresponding to the poly(propylene oxide); and a high temperature transition, corresponding to the polyimide block. Figure 4.3.3.9 shows the dynamic mechanical spectrum for copolymer 1.

In order to develop foams from these materials, the samples were heated in air at 270°C for 10 hours. The density of the foamed films was measured using a density column and these results are provided in Table 4.3.3.4. The density of the films clearly demonstrates the development of porosity. The foaming efficiency obtained by comparing

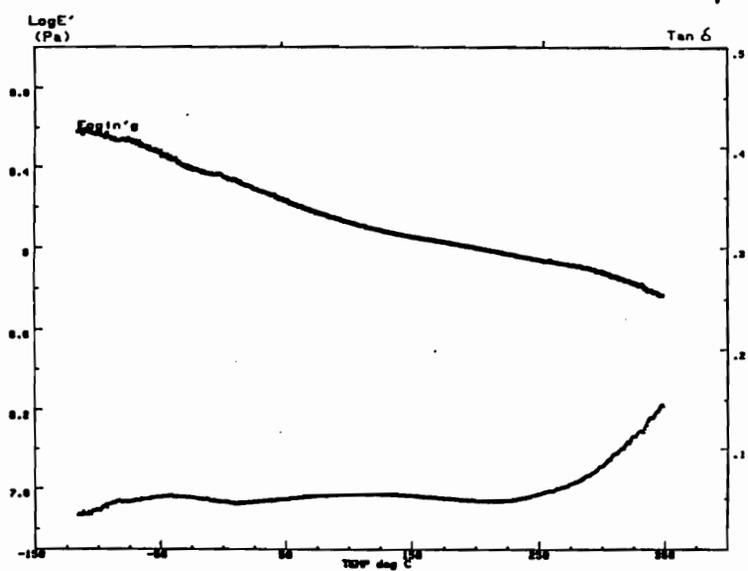
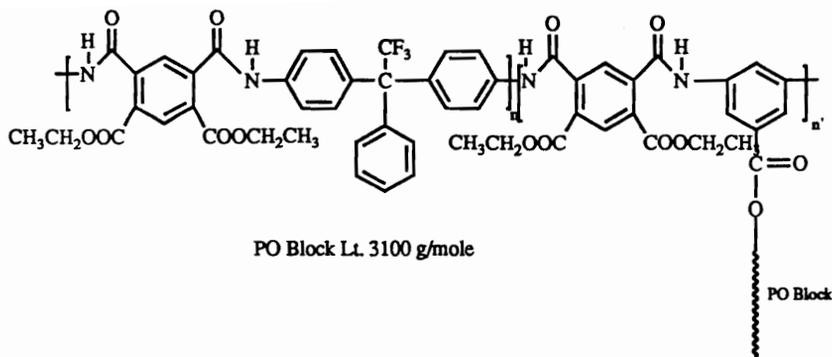


Figure 4.3.3.9 Dynamic Mechanical Spectrum of Polyimide-Poly(propylene oxide)
Copolymer Obtained from Copolymer 1

Table 4.3.3.4 Characteristics of PMDA/3FDA/Polyimide Foams from Poly(amic alkyl ester) Copolymers.

Sample	Composition (wt%)	Density (g/cm ³)	Volume Fraction of Voids (%)
1	19.8	1.13	15.9
2	11.6	1.16	13.4

the volume fraction of voids in the foamed polymer to the volume fraction of poly(propylene oxide) in the unfoamed polymer, indicates about 70% foaming efficiency, which is much less than for foams obtained from fully cyclized polyimides.

TEM was performed on the polyimide - propylene oxide graft copolymer obtained from the poly(amic alkyl ester)s copolymers after the decomposition of the propylene oxide block. The TEM for foamed copolymer 1 is provided in Figure 4.3.2.10. The dark regions in the micrograph correspond to the polyimide matrix. From the micrograph, it is evident that a porous structure was obtained. It is also clear that discrete pores with little or no interconnectivity between the pores had been achieved, similar to the block copolymers. The pore size was observed to range from 50 to 100 Å.

The cellular structure of the foams were also confirmed using SAXS. The SAXS profiles for the unfoamed copolymer 1 and the foamed polyimide film exhibited a well defined peak . The plot of intensity as a function of the scattering vector is shown in Figure 4.3.2.11 for Copolymer 1. The presence of the sharp peak in the case of the unfoamed film also proves the presence of a phase separated morphology, as observed by DMTA. It also indicates that the dispersed poly(propylene oxide) phase has some ordering

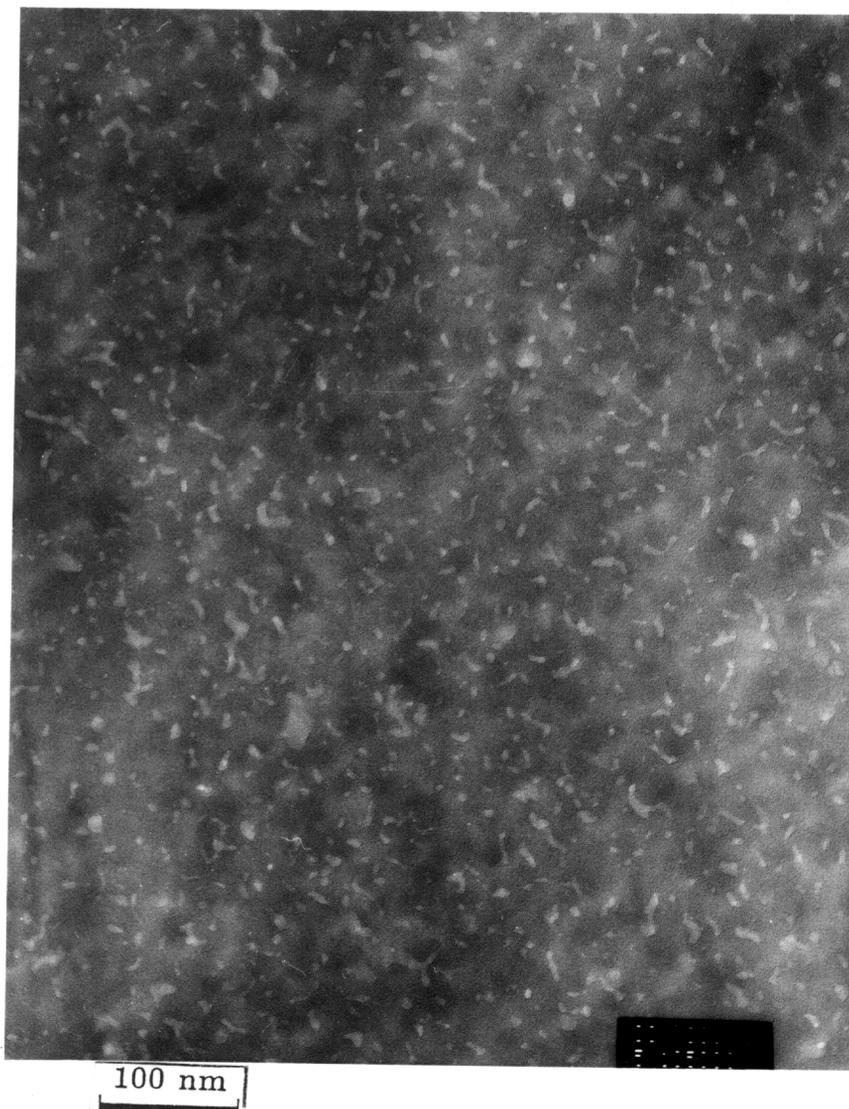


Figure 4.3.3.10 Electron Micrograph of Polyimide nanofoam Obtained from Copolymers 1 after the Poly(propylene oxide) (187, 000 X).

in the polyimide matrix. Once again, the intensity of the SAXS peak was observed to greatly increase on foaming strongly supporting the formation of pores in the polyimide matrix.

The processing of thin films (< 15 microns) by spin coating solutions of PMDA/3FDA /PO poly(amic alkyl ester) copolymers from NMP, provided high quality films on silicon substrates, both with and without an adhesion promoter. Unfortunately, the use of NMP as the processing solvent for thin films on glass results in severe dewetting problems. This impacts the ability to perform the dielectric measurements on the copolymers and foams, since uniform coatings on glass substrates with gold or aluminum metallurgy are required. Several solvents and mixed solvents were used to uniformly coat the polymers. The most effective films were obtained from the DMF/2-ethoxyethyl acetate solvent mixture. No dewetting, orange peeling, or edge build up was found using this system. This cosolvent system was used to successfully prepare samples on silicon substrates for refractive index and thin film stress measurements.

Preliminary thin film stress measurements were performed on the base PMDA/3FDA polyimide and for the polyimide foam obtained from PMDA/3FDA based poly(amic alkyl ester) Copolymers 1 and 2. These materials were processed in parallel on silicon substrates, through the nitrogen cure at 300°C, and foamed (air) at 270°C thermal cycles. The resultant PMDA/3FDA foams had porosity's of 17 and 8 percent respectively. The in-plane stress measurements, as determined by a Flexus stress analyzer at room temperature, showed that foam formation led to a significant reduction in stress. A reduction in stress of 47% for the foam obtained from Copolymer 1, and 21 % obtained from Copolymer 2 was observed. Figure 4.3.3.12 shows a plot of thin film stress as function of temperature for the homopolymer, as well as the foam obtained from Copolymer 1. Foam generation is expected to reduce the modulus according to the volume fraction of voids, while the thermal expansion coefficient is expected to remain the same.

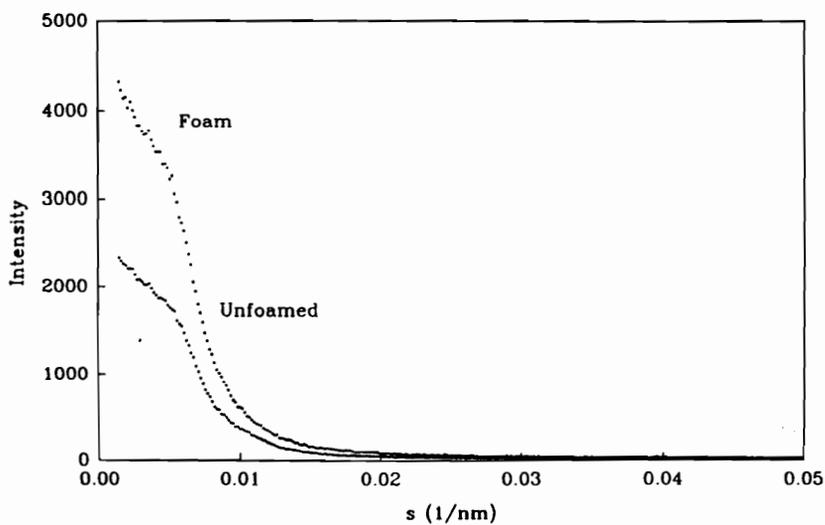
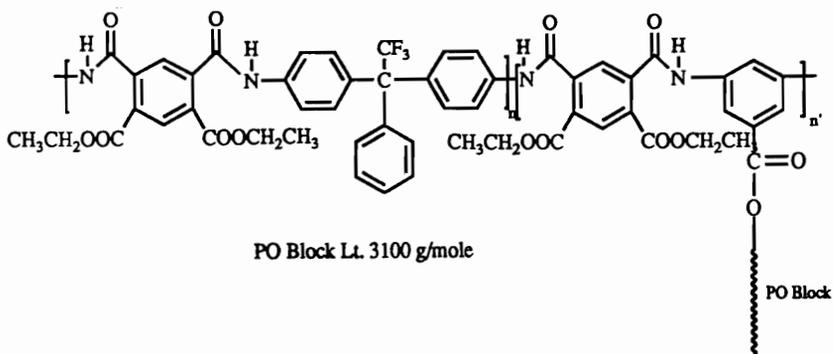


Figure 4.3.3.11 The Plot of Intensity as a Function of the Scattering Vector are Shown for an Unfoamed and Foamed Graft Copolymer 1 .

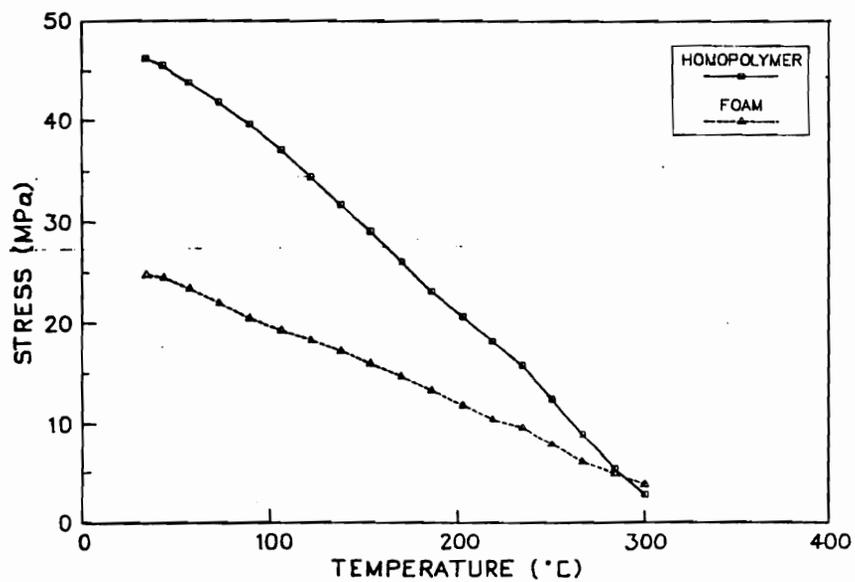
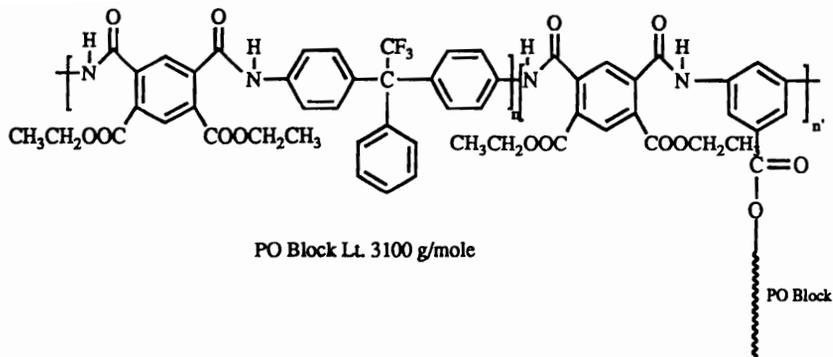


Figure 4.3.3.12 Influence of Nanofoam Structure on Thin Film Stress as a Function of Temperature for Homopolyimide and Polyimide Foam Obtained from Copolymer 1.

Table 4.3.3.5 Refractive Index Measurements on the Polyimide Foams Obtained from Poly(amic alkyl ester) Copolymers Measured at 632.8 nm.

Sample	wt% of poly(propylene oxide)	n (TE)	n (TM)	Change in refractive Index
Homo polyimide	-	1.62	1.60	0.02
1	19.8	1.46	1.42	0.04
2	11.6	1.54	1.51	0.03

Thus, the reduction in modulus is expected to transfer as a reduction in stress consistent with the results observed.

Refractive index measurements were also performed on the homopolyimide and polyimide foams obtained from the poly(amic alkyl ester) copolymers. These results are provided in Table 4.3.3.5.

It can be clearly demonstrated that the refractive index decreases on foaming when compared to the homopolymer. This is the first indication that a decrease in the dielectric constant of the polyimide can be expected on foaming using the approach of thermally degrading a labile block in a high temperature polyimide matrix.

4.3.4 Synthesis and Characterization of crosslinkable polyimide foams

During the development of polyimide nanofoams from completely cyclized polyimides containing poly(propylene oxide) as the labile component, the volume fraction of voids did not quantitatively correspond to the volume fraction of the thermally labile block in the copolymer, particularly for high labile block contents. For the lower poly(propylene oxide) compositions, this can be explained by the various sizes of the poly(propylene oxide) microphase; and that the pressure exerted on a pore ($\approx g / R^2$, where g is the surface tension, and R is the radius) will be higher for small pores causing them to collapse. But in the case of higher poly(propylene oxide) compositions where the collapse was larger, the pressure exerted on the pore, coupled with the interaction of the by-products from the propylene oxide decomposition, was interpreted as plasticization of the polyimide block which resulted in a large scale collapse of the foam. Hence, a polyimide matrix having the same or even higher T_g than the PMDA/3FDA polyimide, which would also interact less with the byproducts from the propylene oxide decomposition would be desirable.

In an attempt to decrease the interaction of the byproducts with the polyimide matrix, and also increase the volume fraction of voids obtainable for the polyimide systems, the use of using a thermosetting polyimide system was attempted. Applying this strategy requires crosslinking at the block or graft copolymer stage so that the network, hence the anticipated stabilization, is present during the foam formation when potential collapse can occur. In addition to the potential for improved foam stability, crosslinking is also expected to improve the inherent solvent resistance of the thermoplastic systems. The drawback of crosslinking is that it can lead to brittle materials. This requires carefully balancing of the degree of crosslinking to obtain materials with good mechanical properties.

Among the many crosslinking chemistries available for high temperature polymers, few have the requisite thermal and mechanical properties. For this investigation, ethynyl groups were chosen as the reactive crosslinkable groups, primarily due to their reactivity and the thermal stability of the resulting crosslinks. The temperature range for the onset of the crosslinking reaction was expected to be between 150 and 300°C, allowing network formation to occur prior to labile block decomposition. In order to obtain an efficient crosslink reaction for such reactive oligomers/polymers, the cure temperature must generally be 20 - 50°C above the T_g of the high temperature polymer. This presents a problem regarding the foam matrices, since the T_g of polyimides is well above the decomposition of the labile block. However, yet foam stabilization requires crosslinking below the decomposition of the labile block. To satisfy these dramatically opposed conditions, methods of plasticizing the matrix during copolymer processing were evaluated. By temporarily lowering the T_g of the matrix, the crosslinking chemistry can take place at temperatures below the decomposition point of the labile block, while the matrix can return to its high T_g state after removing the plasticizing agent. To facilitate this, two approaches were tested: the use of a high boiling cosolvent such as NMP, and the use of a poly(amic alkyl ester) precursor to the polyimide matrix. In the former, the high

boiling solvent is expected to sufficiently suppress the matrix T_g , allowing crosslinking to occur in the desired temperature range. In the case of the poly(amic alkyl ester) precursor, the meta isomer of PMDA/3FDA has already been shown to undergo a significant softening in the required temperature range, so that the necessary chemical reactions, e. g., chain extension can occur. It was also anticipated that crosslinking would be similarly benefited by this behavior of the poly(amic alkyl ester).

In order to apply the ethynyl chemistry with high T_g PMDA/3FDA systems prior to developing foam, ethynyl terminated low molecular weight oligomers of PMDA/3FDA fully cyclized polyimide and meta-poly(amic alkyl ester) were synthesized and characterized. The 3-ethynyl aniline terminated PMDA/3FDA polyimide matrix resins were synthesized using a conventional two-step polyimide process. The reaction scheme for the synthesis of the 3-ethynyl aniline terminated PMDA/3FDA polyimide is provided in Figure 4.3.4.1. In the first step poly(amic acid) was prepared by adding the dianhydride to a stirred solution of the diamine and endcapped these with 3-ethynyl aniline under ambient temperatures. The poly(amic acid) was subsequently converted to polyimides by adding acetic anhydride / pyridine mixture and stirring for 6-8 hours at 70°C under nitrogen. By adding stoichiometric amounts of 3-ethynyl aniline based on Carother's equation, PMDA/3FDA based polyimides of 3 different molecular weights were synthesized ranging from 3000 g/mole to 12000 g/mole.

As shown in Table 4.3.4.1, good molecular weight control was achieved utilizing 3-ethynyl aniline as an endcapping agent. These materials were confirmed to be completely imidized by the detection of strong infrared imide absorption's at 1780 cm^{-1} , 1730 cm^{-1} , 1370 cm^{-1} , 710 cm^{-1} , as well as by the absence of amic acid related absorption's. In addition, the 2130 cm^{-1} characteristic of the ethynyl stretch, though not strong, was observed for these materials.

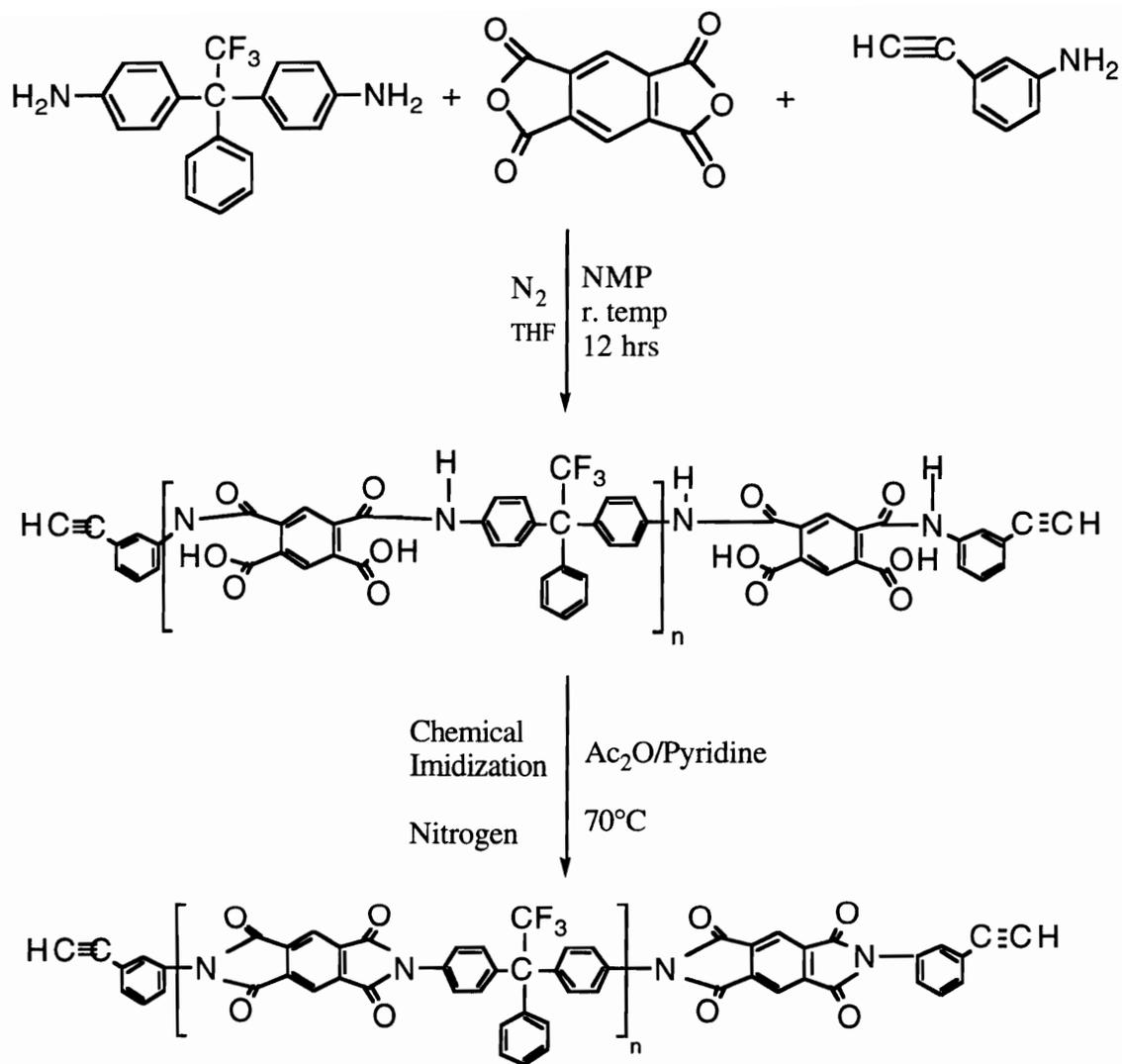


Figure 4.3.4.1 Synthesis of 3-Ethynyl Aniline Terminated PMDA/3FDA/Polyimides

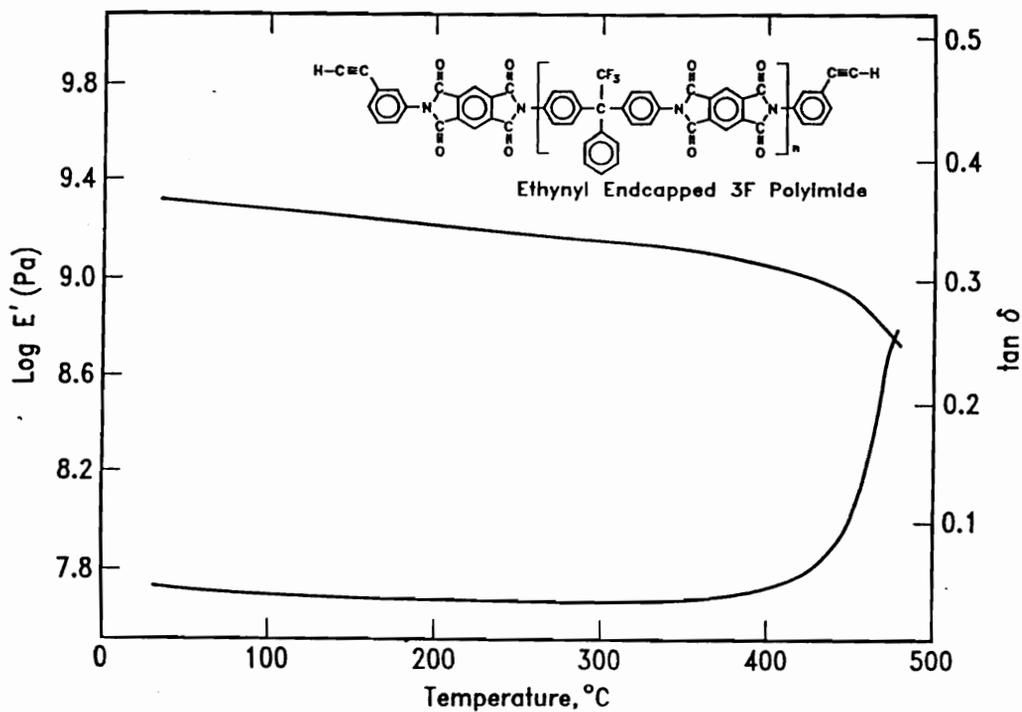


Figure 4.3.4.2 Dynamic Mechanical Analysis Spectrum of Crosslinked Polyimide Obtained from 3-Ethynyl Terminated PMDA/3FDA Polyimide. (Mol. Wt. of Polyimide = 3000 g/mole)

Table 4.3.4.1 Characteristics of Ethynyl Terminated Polyimide Oligomers and Crosslinked Polyimide Films

Sample	Molecular Weight of oligomers before cure (g/ mole)		T _g of cured polyimide	Intrinsic Viscosity	Thermogravimetric °C)	
	Target	Obtained (¹ H NMR)	DMTA(°C)	NMP,(dl/g), 25°C	air	Nitrogen
1	3000	4600	460	0.15	500	524
2	6000	6075	410	0.18	510	526
3	10000	9800	420	0.22	490	521

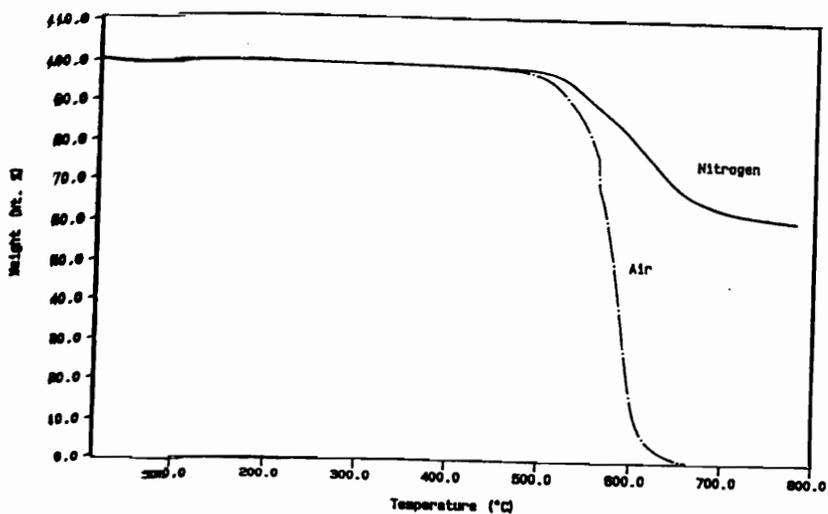
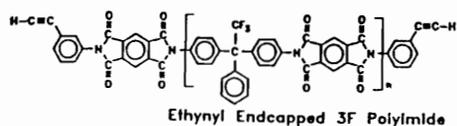


Figure 4.3.4.3 The TGA Thermogram of Crosslinked Polyimides Obtained Both in Air and Nitrogen

Cured thin films of these materials were prepared by dissolving them materials in NMP at about 15% solids and casting these on to a glass plate. The films on glass were heated for 1 hour at 100 and 200°C under nitrogen. The final curing of the samples were prepared at different times (1 to 3 hours) at 300°C. Although the films were observed to be brittle and no T_g could be detected by DSC for them up to 400°C. DMTA measurements performed in air on all the cured films were performed from 30 to 475°C at a rate of 10°C/min. The T_g were observed to range from 410 to 460°C for these materials, as shown in Table 4.3.4.1. These results are comparable to the T_g of the high molecular weight systems. The dynamic mechanical results for cured film obtained from ethynyl terminated 3000 g/mole oligomer is shown in Figure 4.3.4.2.

Thermal stability of the cured PMDA/3FDA/3-ethynyl terminated polyimides was also investigated. The crosslinked polyimides exhibited 5% weight loss values at temperatures ranging from 480 to 520°C, which is consistent with most polyimide systems. Dynamic TGA spectrum of cured films obtained from ethynyl terminated 3000 g/mole oligomer is shown in Figure 4.3.4.3. The cured polymers were subjected to isothermal gravimetric analysis for 12 hours at 310°C under air atmosphere. These materials exhibited a 1-3% loss in weight under these conditions.

These results were extremely encouraging and indicated the successful synthesized of high T_g crosslinked PMDA/3FDA polyimides. However when the efficiency of the network formation was evaluated by immersing a cured polyimide films in NMP, the films lost their mechanical integrity within a short period of time. In addition, the cured films were observed to be brittle. Thus, the curing of the ethynyl terminated PMDA/3FDA polyimide oligomer resulted in films which were not creasable and also exhibited poor solvent resistance. These results indicate that while a thermal crosslinking reaction via ethynyl groups was occurring, it was not proceeding very efficiently. These results were anticipated for the high T_g polyimide oligomers and polymers. Unlike traditional systems,

polyimides with high glass transition temperatures ($T_g > 350^\circ\text{C}$) have been shown to lack the expected tracking of the T_g with curing temperatures.¹⁷⁴ Upon initial curing the ethynyl groups at around 200°C , with the simultaneous removal of the solvent, the T_g of the polyimide is expected to jump very quickly to its maximum value, thus vitrifying the system and preventing it from displaying sufficient chain mobility in this temperature regime. This vitrification prevents any possible crosslinking reaction from occurring, thus resulting in lightly crosslinked brittle materials with poor solvent resistance.

Alternatively, one can easily circumvent this problem of system vitrification by the use of poly(amic alkyl ester) as the T_g of the poly(amic alkyl ester) would be much lower than the corresponding polyimide system. Also, by choosing the appropriate isomer of the diester diacylchloride of PMDA, the T_g of the poly(amic alkyl ester) can be further lowered (meta isomer has lower T_g than the corresponding para isomer). There are several other advantages of using the poly(amic alkyl ester) to obtain crosslinked matrices over to the same crosslinked materials produced from respective poly(amic acids) or polyimides. The use of poly(amic alkyl ester)s has been shown to elevate the imidization temperature up by about 100°C , and also to broaden the imidization temperature regime in comparison to the imidization reaction of the corresponding poly(amic acids). For example, when using of poly(amic ethyl esters) in the PMDA/ODA system, the maximum imidization temperature was observed at 255°C with an imidization temperature range of 240 to 350°C . Thus, increasing the imidization temperature, should result in a higher crosslinking reaction to occur at temperature below the major imidization temperature due to the fact that the poly(amic alkyl ester)s would be in a softened state. In addition, this broad imidization temperature range would result in the evolution of ethanol, which is capable of plasticizing the polymer matrix over a large temperature range, thus permitting for a broader processing window for crosslinking reactions to occur. By shifting to a higher imidization temperature

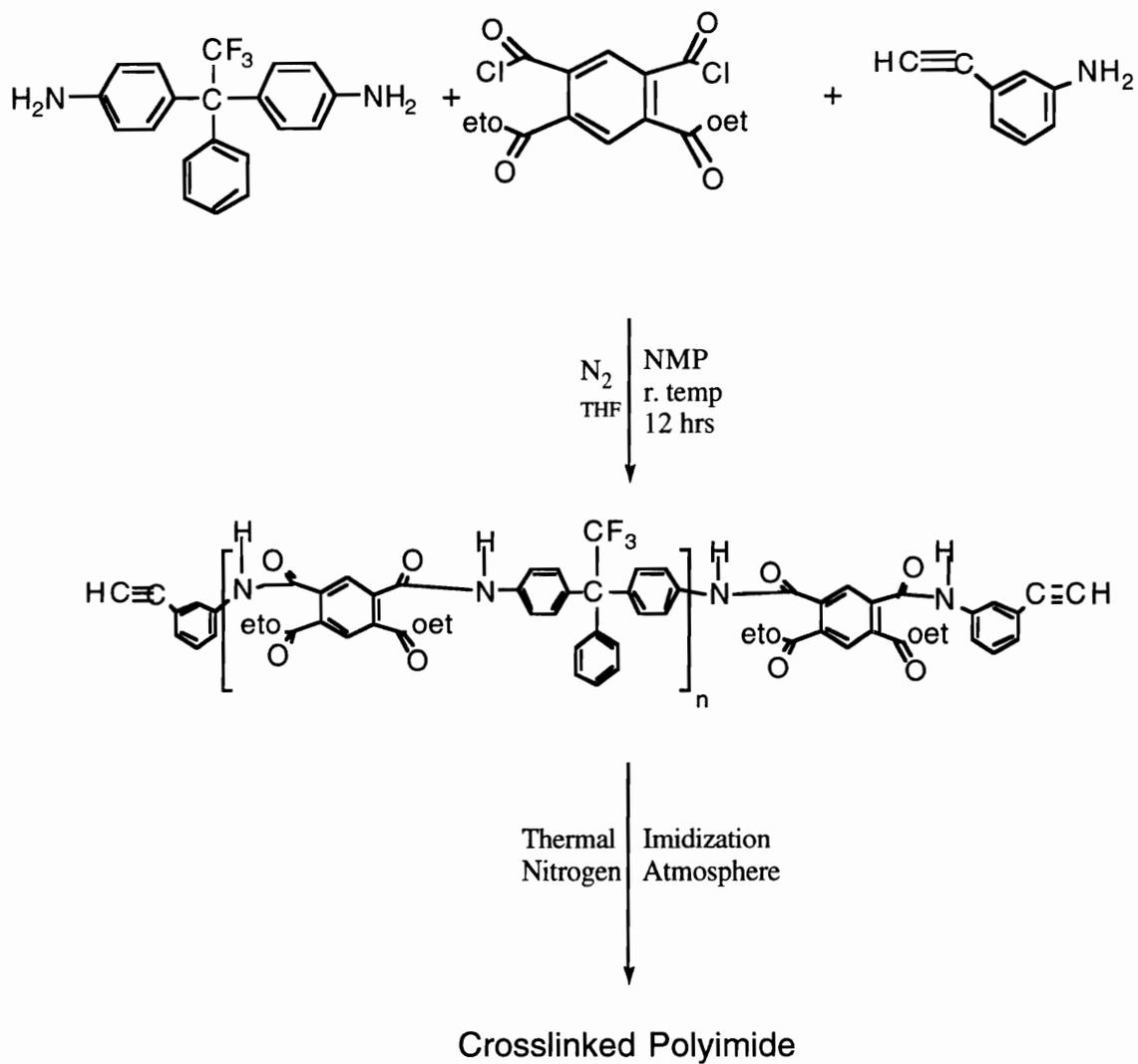


Figure 4.3.3.4 Synthesis of 3-Ethynyl Aniline Terminated Poly(amic alkyl ester) Oligomers

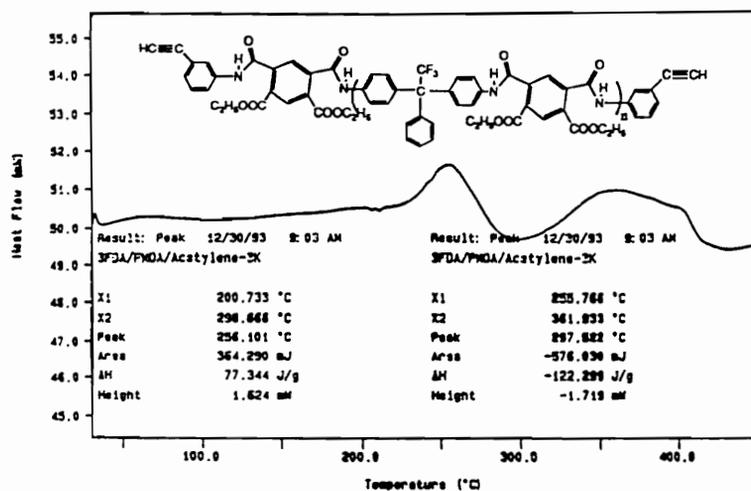
Table 4.3.4.2 Characteristics of Ethynyl Terminated Poly(amic alkyl ester) Oligomers and Crosslinked Polyimide Films

Sample	Molecular Weight of ethynyl terminated poly(amic alkyl ester) oligomers (g/mole)		T _g cured polyimide DMTA(°C)	Intrinsic Viscosity NMP,(dl/g), 25°C	Thermogravimetric (°C)	
	Target	Obtained (¹ H NMR)			air	Nitrogen
1	3000	3500	> 450	0.13	501	520
2	6000	5450	> 450	0.15	504	526
3	10000	10200	> 450	0.19	510	521

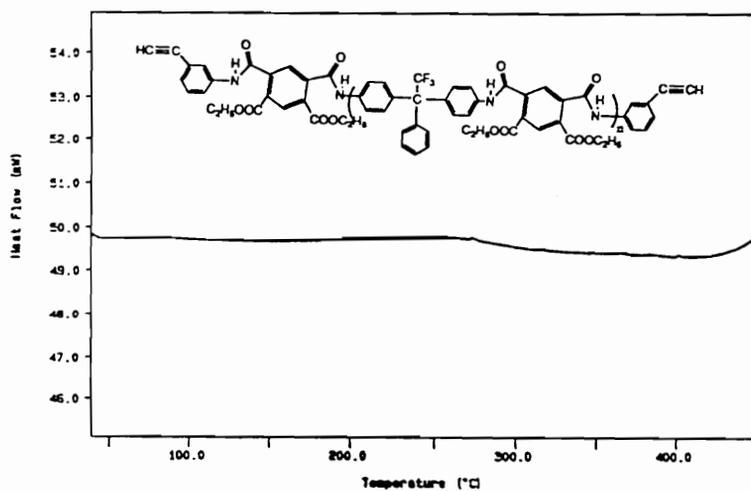
separation of the solvent evaporation process from the imidization process becomes possible, minimizing the potential for void formation. The use of the ethyl ester instead of isopropyl or t-butyl ester also result, in reduced polymer shrinkage, due to the small size of the alkyl group, although some amount of shrinkage is expected to occur upon crosslinking.

Based on these advantages, poly(amic alkyl ester)s of PMDA/3FDA endcapped with 3-ethynyl aniline were synthesized. The reaction scheme for the synthesis of ethynyl terminated poly(amic alkyl ester) is provided in Figure 4.3.4.4. The synthesis involved the incremental addition of diethyl ester diacyl chloride of PMDA (meta isomer) in dry THF to a solution of 3-ethynyl aniline and 3FDA in NMP containing pyridine as the acid acceptor. The solid composition was maintained at 15% for each polymerization. The solution was stirred under nitrogen for 12 hours, after which the polymers were isolated in the methanol/water mixture, rinsed with water and methanol and vacuum dried at 50°C. By adding appropriate amounts of the monofunctional endcapper 3-ethynyl aniline, PMDA/3FDA based poly(amic alkyl ester) of 3 different target molecular weights were synthesized, ranging from 3000 g/mole to 12000 g/mole. As evidenced from Table 4.3.4.2, good molecular weight was achieved. Intrinsic viscosity measurements of these poly(amic alkyl esters) were obtained in NMP and these results are also reported in Table 4.3.4.2.

Differential scanning calorimetric (DSC) study of the above ethynyl terminated poly(amic alkyl ester)s was performed under nitrogen atmosphere from room temperature to 450°C, at a scan rate of 10°C/min. All the compounds exhibited two transitions: a) an imidization endotherm of the polyimide precursor poly(amic alkyl ester) followed by b) an immediate exotherm corresponding to ethynyl crosslinking reaction on the first scan. The samples were then quenched to room temperature and a second scan was performed. On the second scan, both the endothermic imidization transition and the exothermic transition



First Heat



Second Heat

Figure 4.3.4.5 The First and the Second DSC Scan of 3000 g/mole Ethynyl Terminated Poly(amic alkyl ester) Oligomer

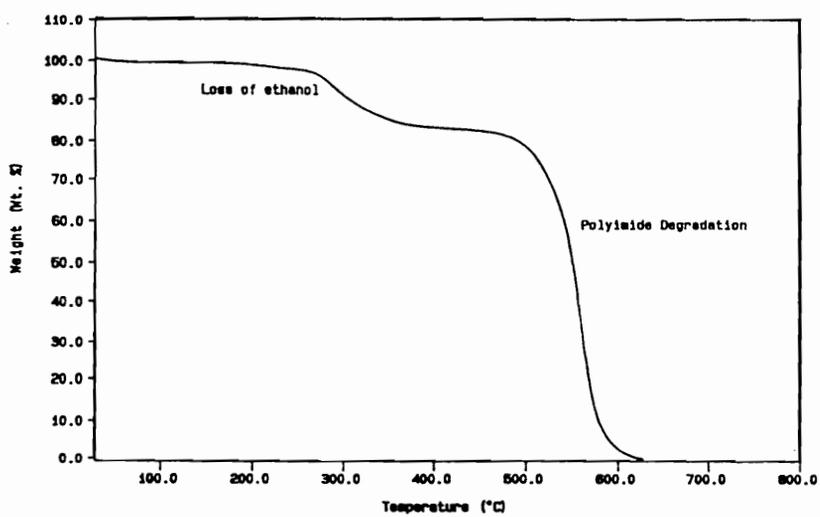
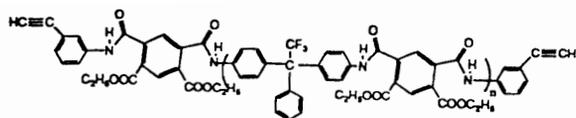


Figure 4.3.4.6 The TGA Spectrum of Poly(amic alkyl ester) Obtained in Air

arising from the ethynyl cure reaction were found to be absent indicating high conversion of both the imidization and crosslinking reaction. Figure 4.3.4.5 shows both the first and the second DSC scan of 3000 g/mole ethynyl terminated poly(amic alkyl ester) oligomers. It is very difficult to identify exactly where the onset of imidization and crosslinking begins to occur, as the spectrum is complicated by the fact that both the ring closure reaction of the alkyl ester to imide and the ethynyl groups start to undergo thermal reaction at around 200°C.

In order to separate the two processes, two experiments were performed. First dynamic thermogravimetric analysis (TGA) of the poly(amic alkyl ester) was conducted from 30 to 800°C at a heating rate of 10°C/min. in both nitrogen and air atmosphere. All the compounds exhibited a two-step weight loss profile, where the first step corresponds to the loss of ethanol arising from the imidization reaction of the poly(amic alkyl ester), and the second step corresponds to the degradation of the polyimide. Though crosslinking reactions of the ethynyl groups are expected as the temperature is raised no volatiles should arise on curing of the ethynyl groups. Thus, by following the onset and end of the initial weight loss step arising due to the evolution of ethanol, it should be feasible to obtain the imidization temperature range of the poly(amic alkyl ester) to the corresponding polyimide. In fact, from TGA the onset of the imidization reaction for the PMDA/3FDA based meta-poly(amic alkyl ester) at 185°C, while the imidization reaction was recorded at 385°C. The TGA spectrum of poly(amic alkyl ester) obtained both in air and nitrogen, is provided in Figure 4.3.4.6.

Similarly, in order to separate the imidization reaction and track only the ethynyl cure reaction, ESR spectroscopy was used. Ethynyl terminated materials are known to undergo thermal crosslinking reaction via a free radical mechanism. Thus, when poly(amic alkyl ester)s are thermally heated to around 200°C, ethynyl bonds are expected to cleave, resulting in the formation of carbon-centered free radicals, and the crosslinking reaction is

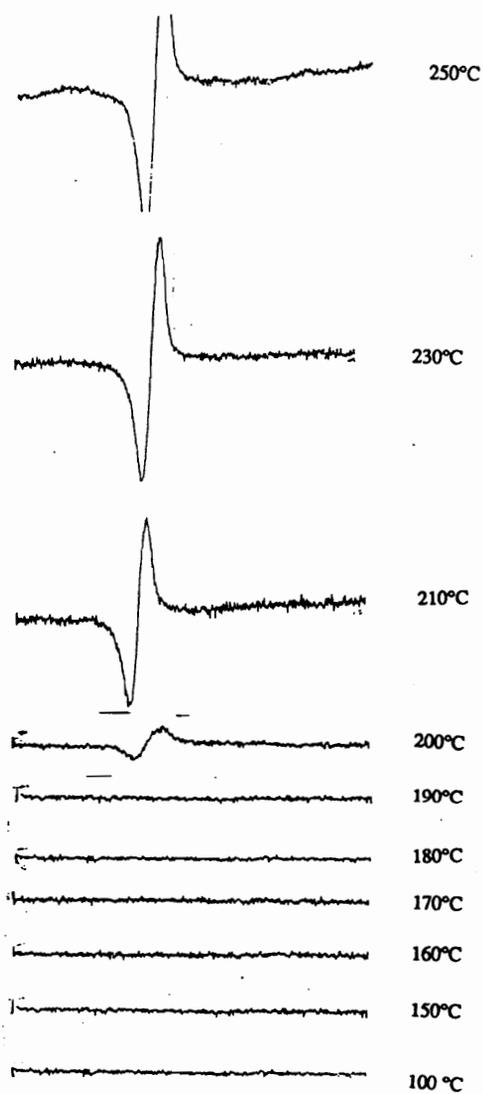


Figure 4.3.4.7 Electron Spin Resonance Spectroscopic Results of Poly(amic alkyl ester) Endcapped with Ethynyl Groups as a Function of Temperature

expected to occur in these materials. The formation of the free radicals on heating the poly(amic alkyl ester) should be completely independent of the imidization reaction, and that the ESR spectra should be sensitive only to the crosslinking reaction. From ESR experiment it should be possible to pinpoint the onset of the ethynyl cure reaction temperature, independent of the imidization temperature. ESR spectrums were obtained on solid samples contained in a tube sealed under vacuum. The sample was heated to different temperatures from room temperature using a Bruker variable temperature heater. The sample was held constant for a few seconds for the temperature to equilibrate and the ESR scan was performed. These results are provided in Figure 4.3.4.7. It can be clearly observed that the first appearance of the carbon centered free radical in the poly(amic alkyl ester) occurs between 180 and 190°C, and the intensity of the radical was seen to increase up to 250°C. Based on these results, it is clear that the onset of the crosslinking reaction of the ethynyl groups occurs around 190°C; this is almost the same temperature at which the imidization process begins.

Dynamic mechanical behavior of the cured polyimide films from the ethynyl-terminated 3000 g/mole poly(amic alkyl ester)s oligomer is shown in Figure 4.3.4.8 as a function of temperature. In order to study the effect of the molecular weight of the ethynyl terminated poly(amic alkyl ester) on the properties of the cured polyimide, solution cast films of three different molecular weight poly(amic alkyl ester) samples endcapped with an ethynyl group were prepared. These films were heated to 300°C and held for 2 hours. DMA measurements were performed in air on the cured films from 30 to 450°C at a rate of 10°C /min and a frequency of 1 Hz.

Up to 450°C, the samples did not show any drop in storage modulus or a tan δ peak, suggesting that the cured materials had a T_g exceeding this value. These results are provided in Table 4.3.4.2. In order to study the effect of curing time on properties of the crosslinked material, two different samples of the 3000 g/mole poly(amic alkyl ester)

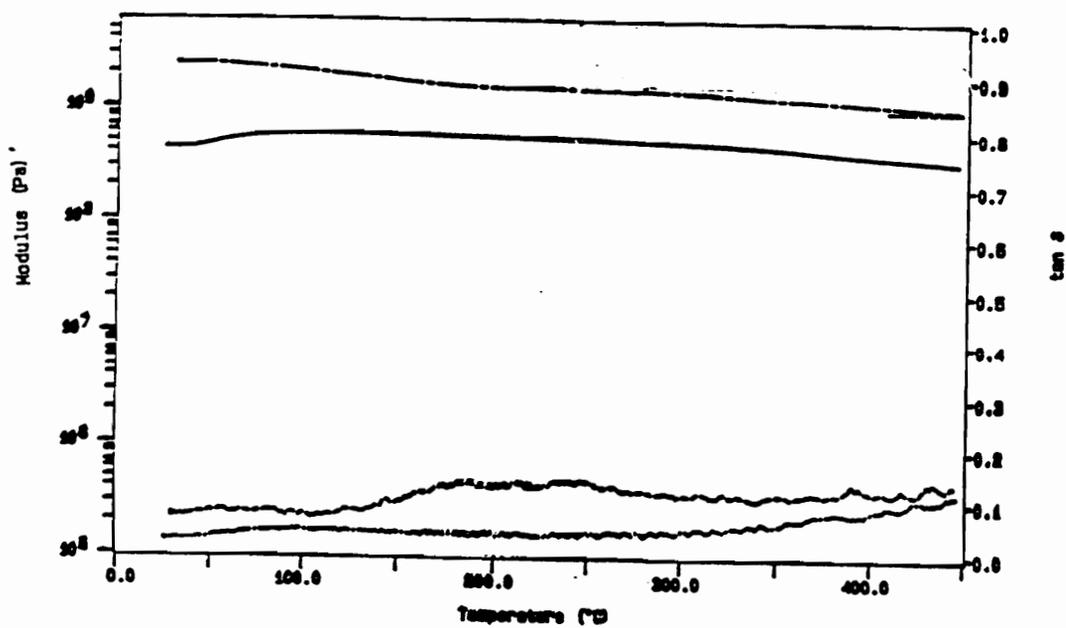
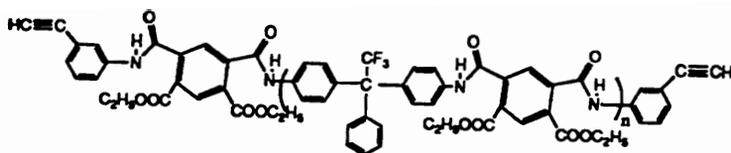


Figure 4.3.4.8 Dynamic Mechanical Behavior of the Cured Polyimide Films From the Ethynyl Endcapped Poly(amic alkyl ester)s

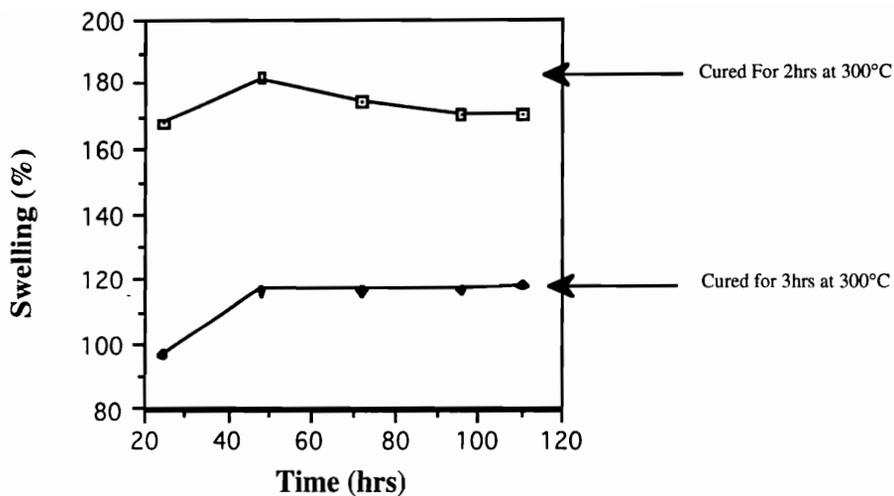


Figure 4.3.4.9a The Effect of Curing Time at 300°C on Swelling (wt/wt) in NMP of the Crosslinked Polymer Obtained from 3000g/mole Poly(amic alkyl ester)Oligomer

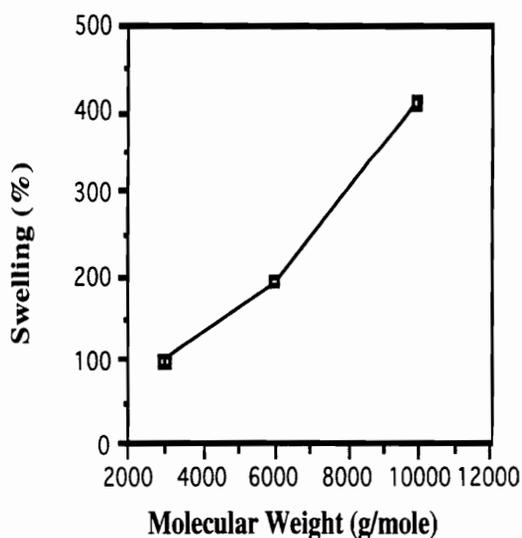


Figure 4.3.4.9b The Effect of Molecular Weight of the Ethynyl Endcapped Poly(amic alkyl ester) on Swelling(wt/wt) in NMP Characteristics of a Crosslinked Polyimide

oligomers were heated to 300°C and held for 2 hours and 3 hours, respectively. The cured films were then lifted off by scoring the edges and immersing them in water. The films were observed to be tough and creasable upon curing. DMA measurements performed on these samples did not show any difference between the two samples. Both samples were still observed to have a T_g higher than 450°C.

Solvent resistance studies on all the crosslinked polyimide samples obtained from the poly(amic alkyl ester)s were performed by immersing the cured films in NMP for up to 5 days. In general the lower the molecular weight of the poly(amic alkyl ester) endcapped with the ethynyl groups, the better the solvent resistance, due to higher crosslink density upon curing. The solvent resistance was observed to be better with longer curing time at 300°C. Figure 4.3.4.9a shows the effect of curing at 300°C on swelling of the crosslinked polymer obtained from 3000 g/mole poly(amic alkyl ester) oligomer and Figure 4.3.4.9b shows the effect of molecular weight of the ethynyl endcapped poly(amic alkyl ester) on the swelling characteristics of a crosslinked polyimide.

The thermal stability of these materials were similar to both the high molecular weight linear analog and the crosslinked polyimides obtained from the ethynyl terminated polyimide oligomers.

Having successfully synthesized and characterized crosslinked polyimides via terminal ethynyl groups, poly(amic alkyl ester) copolymers containing pendant ethynyl groups were synthesized in order to understand the structure-property relationships of crosslinked polyimides obtained via either terminal crosslinking or pendant crosslinking. In order to synthesize poly(amic alkyl ester)s containing pendant ethynyl groups, a diamine containing pendant ethynyl groups had to be synthesized. 1,1bis(4aminophenyl)-1-(4-ethynylphenyl)-2,2,2-trifluoroethane(EDA) was synthesized based on the work of Jensen and Hergenrother.¹⁷⁵ Using diamine as a source of the pendant ethynyl groups, copolymers were synthesized with 10, 20 or 40 mol% of the diamine containing the

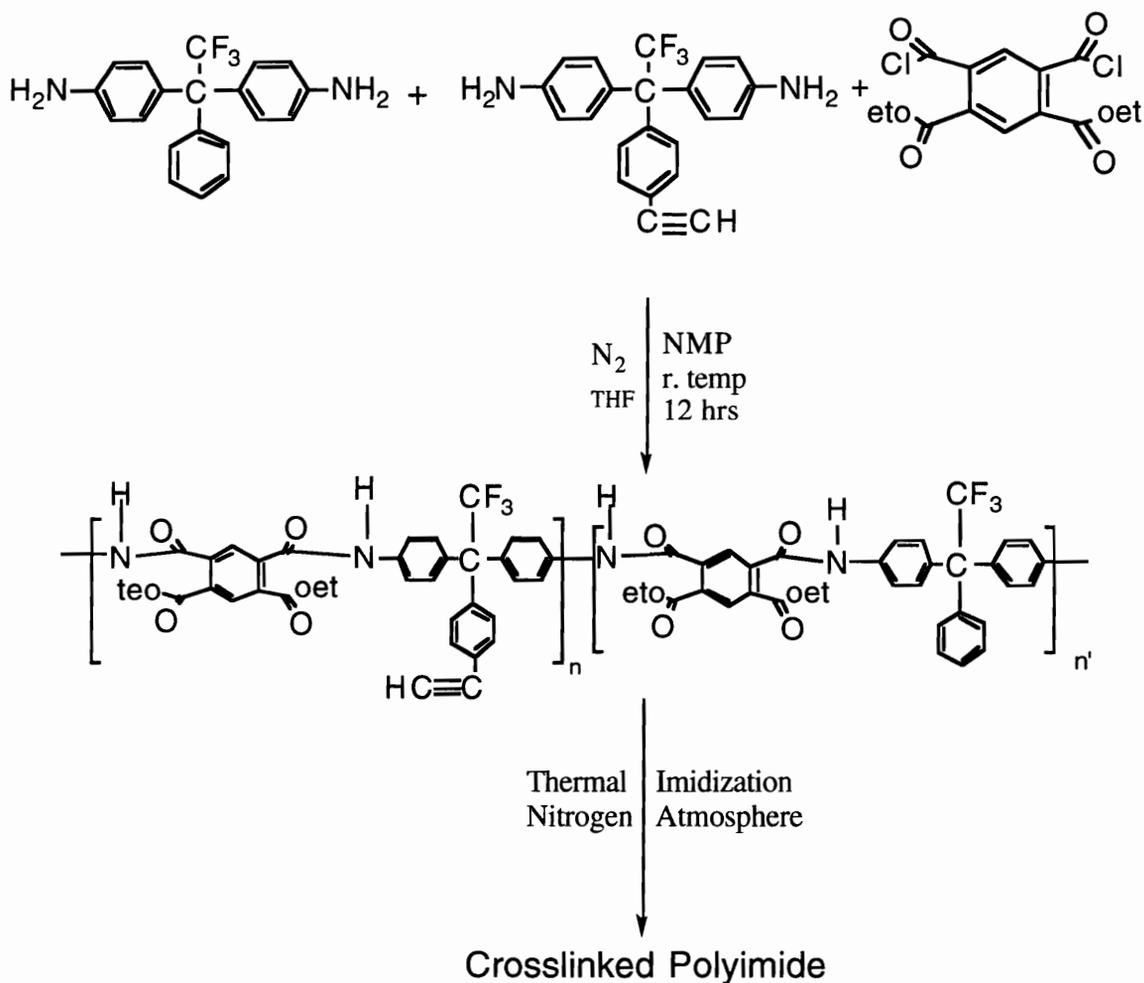


Figure 4.3.4.10 Synthesis of PMDA/3FDA Based Poly(amic alkyl ester) Containing Pendant Ethynyl Groups.

pendant ethynyl group and remaining 90,80 or 60 mol% respectively of the 3FDA diamine (without a pendant ethynyl group) was used. Poly(amic alkyl ester)s were synthesized via the incremental addition of diethyl ester diacyl chloride of PMDA (meta isomer) in dry THF to a solution of EDA and 3FDA in NMP containing pyridine as the acid acceptor. The reaction scheme for the synthesis of the poly(amic alkyl ester) containing pendant ethynyl groups is provided in Figure 4.3.4.10. The solid composition was maintained at 15% for each polymerization. The solution viscosity was observed to increase dramatically and the solution was further stirred under nitrogen for 12 hours, after which the polymers were isolated in the methanol/water mixture, rinsed with water and methanol, and vacuum dried at 50°C. By adding appropriate amounts of the EDA, PMDA/3FDA based poly(amic alkyl ester) containing 3 different mole ratios of the pendant ethynyl groups, polymer were synthesized ranging from 10 mol% to 40 mol% as evidenced from Table 4.3.4.4. High intrinsic values, indicating the synthesis of high molecular weight poly(amic alkyl ester)s reflects the purity of the monomers used in the polymerization.

Dynamic mechanical behavior of the cured polyimide films from the pendant ethynyl poly(amic alkyl ester)s is shown in Figure 4.3.4.11 as a function of temperature. In order to observe the effect of % pendant ethynyl functionality's on the properties of the cured polyimide, films containing 10, 20 and 40 mole% of the ethynyl group were prepared from NMP at about 10% concentration and cast on to a glass plate. These samples were heated to 300°C and held for 3 hours. All the resulting cured films were tough and creasable. DMTA measurements were performed in air on the cured films from 30 to 450°C at a rate of 10°C /min. These results are provided in Table 4.3.4.3. The T_g of the crosslinked polyimide obtained from the precursor poly(amic alkyl ester) containing 10 mol% of the pendant ethynyl groups was observed around 430°C comparable to that of the high molecular weight linear PMDA/3FDA polyimide; while the crosslinked polyimide obtained from the precursor poly(amic alkyl ester) containing 20 and 40 mol% of the

Table 4.3.4.3 Characteristic of PMDA/3FDA Based Poly(amic alkyl ester) Containing Pendant Ethynyl Groups

Sample	Mole % of Pendant Ethynyl Groups	T _g DMTA (°C)		Thermogravimetric Analysis (°C)	
		Before Crosslinking	After Crosslinking	Air	Nitrogen
1	10	-	430	500	524
2	20	-	> 450	510	526
3	40	-	> 450	490	521

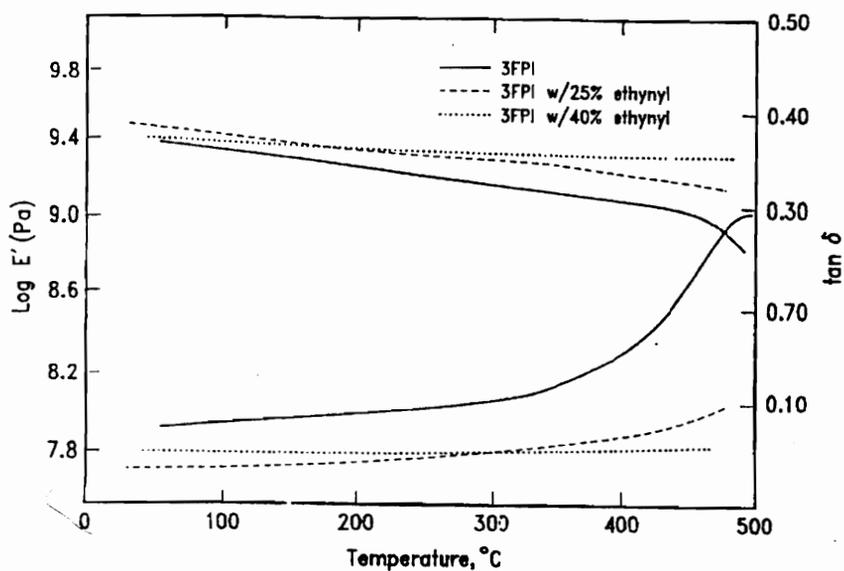
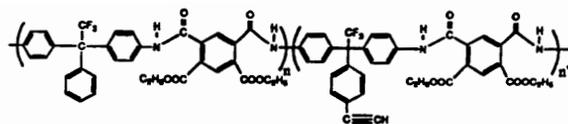


Figure 4.3.4.11 Dynamic Mechanical Behavior of the Cured Polyimide Films From the Pendant Ethynyl Poly(amic alkyl ester)s

pendant ethynyl groups, was greater than 450°C. These results are very similar to those obtained for crosslinked polyimides from terminal ethynyl groups.

Solvent resistance on all the crosslinked polyimide samples obtained from the poly(amic alkyl ester)s were determined by immersing the cured films in NMP. In general, the poly(amic alkyl ester) containing higher mole% of the ethynyl groups exhibited better solvent resistance, due to higher crosslink density present in the sample. Figure 4.3.4.12 shows the effect of mole % of pendant ethynyl groups present in poly(amic alkyl ester) on the swelling characteristics of a crosslinked polyimide. It should also be noted that polymers with pendant ethynyl groups show better solvent resistance than the crosslinked polyimides obtained from terminal ethynyl groups.

The thermal stability of the crosslinked polyimides obtained from poly(amic alkyl ester)s containing pendant ethynyl groups was observed to be similar to that of both the high molecular weight linear analog, and the polyimide obtained from t-butyl endcapped poly(amic alkyl ester)s homopolymers.

Thus, having synthesized and characterized both the end functionalized and pendant ethynyl based PMDA/3FDA poly(amic alkyl ester) resins, the next step in order to generate foams was to synthesize ethynyl containing poly(amic alkyl ester) copolymers. With regards to the ethynyl endcapped PMDA/3FDA, diamine terminated poly(propylene oxide) was used to generate graft copolymers, while mono-amine terminated poly(propylene oxide) was used to produce block copolymers with regards to the poly(amic alkyl ester) copolymers containing pendant ethynyl groups.

Two different diamino benzoate block lengths were investigated (3100 and 4100 g/mole) at compositions of 25% for 3100 g/mole poly(propylene oxide) oligomer and 15, 25 and 40% compositions for the higher 4100 g/mole oligomer for generating graft copolymers endcapped with ethynyl groups. Based on the previous results it was determined that the highest solvent resistance was obtained for 3000 g/mole poly(amic alkyl

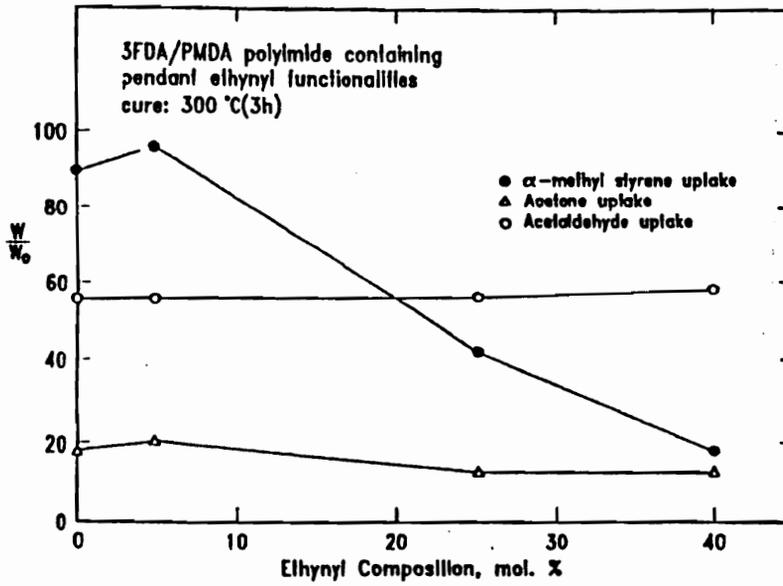
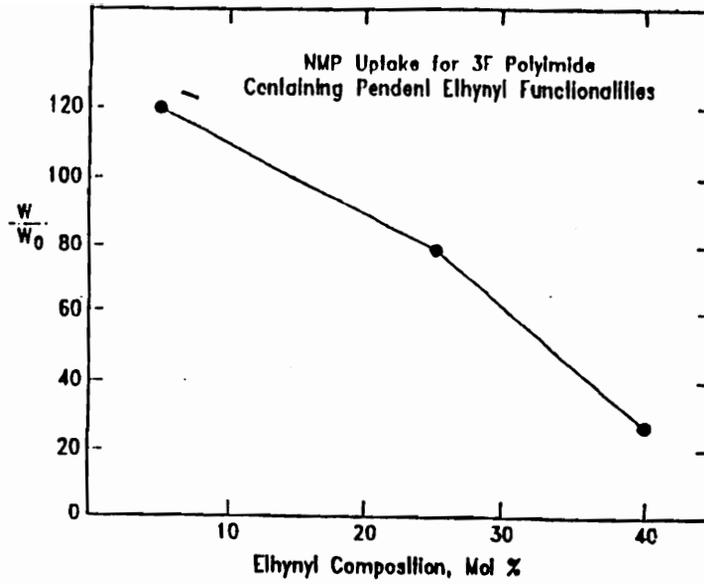


Figure 4.3.4.12 The Effect of Mole % of Pendant Ethynyl Groups Present in Poly(amic alkyl ester) on Swelling Characteristics of a Crosslinked Polyimide

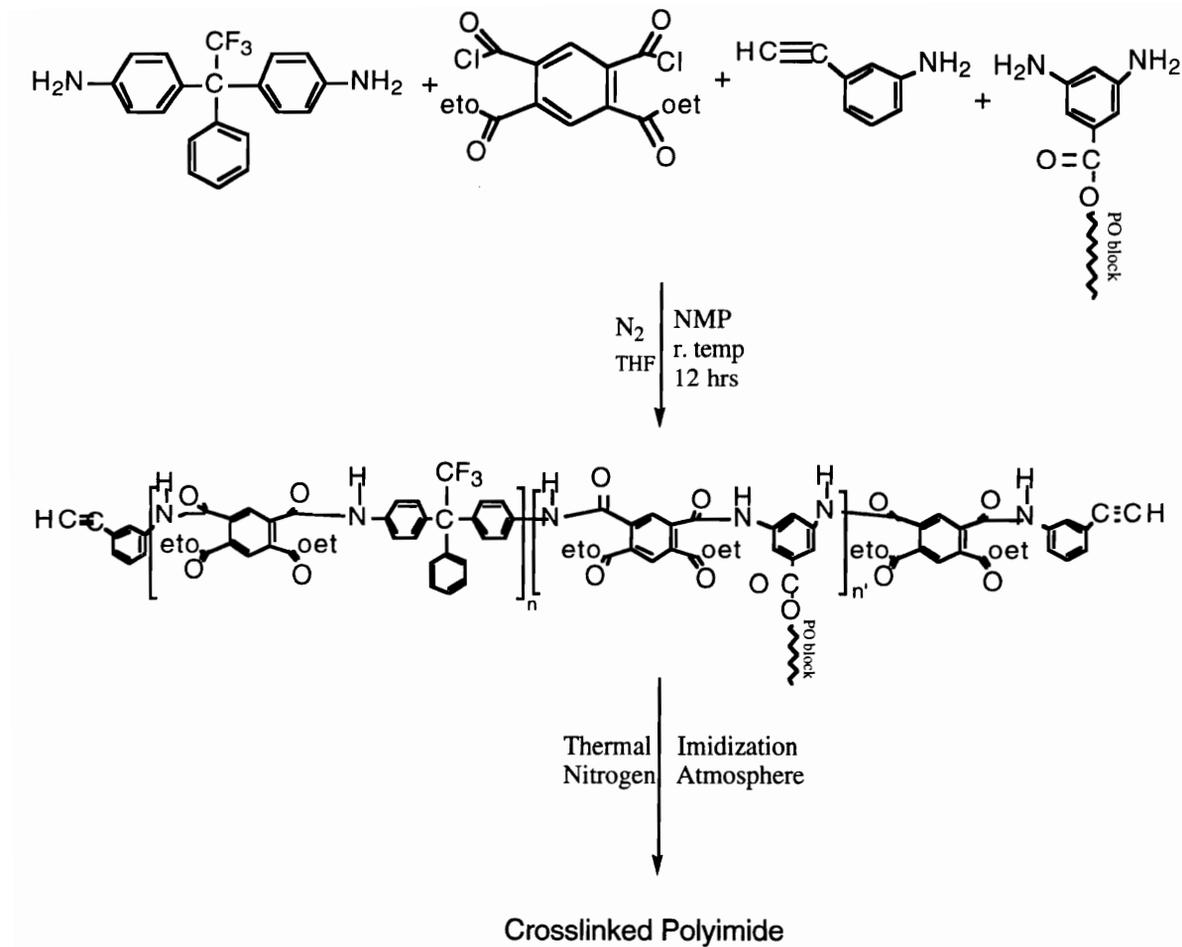


Figure 4.3.4.13 Synthesis of Ethynyl Terminated PMDA/3FDA/Poly(propylene oxide) Graft Copolymers

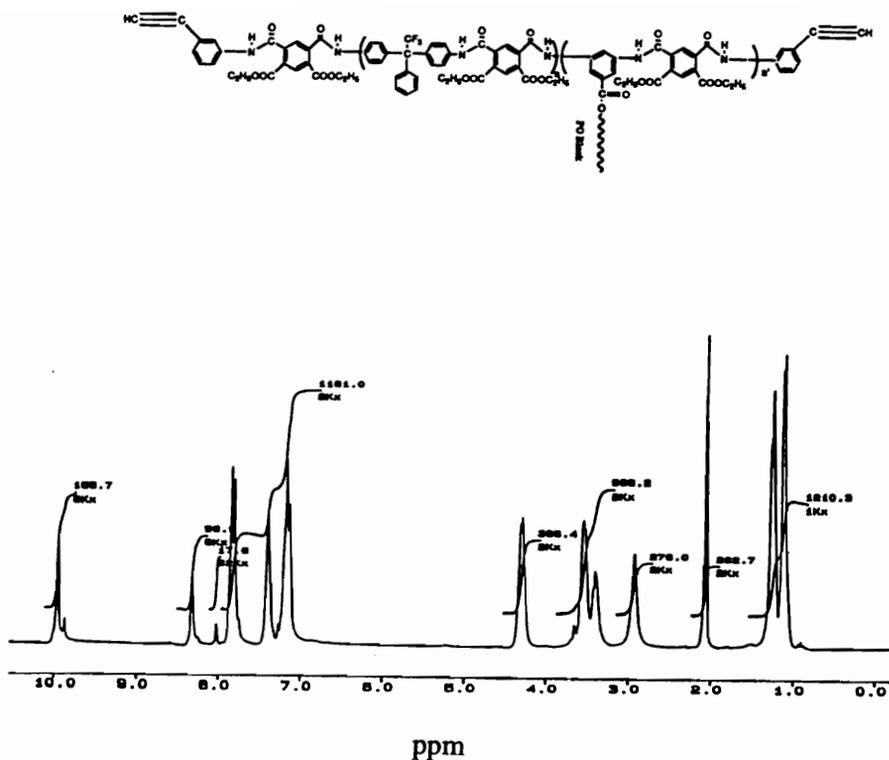


Figure 4.3.4.14 ¹H NMR of the Ethynyl Terminated Poly(amic alkyl ester) Copolymer of mol.wt. 3000 g/mole Containing 25 wt.% of the Poly(propylene oxide) Block of Molecular Weight 3100 g/mole

Table 4.3.3.4 Characteristics of meta-Poly(amic alkyl ester) of PMDA/3FDA /Poly(propylene oxide) Copolymers. A as Prepared Sample and B Obtained From Polyimide Film before Foaming

Sample	Poly(propylene oxide) mol. wt.	Target	Obtained From ¹ H NMR		From TGA
			A	B	
1	3100	25	19.8	15.7	19.0
2	4100	15	14	-	13
3	4100	25	19.5	-	18
4	4100	40	38.5		37

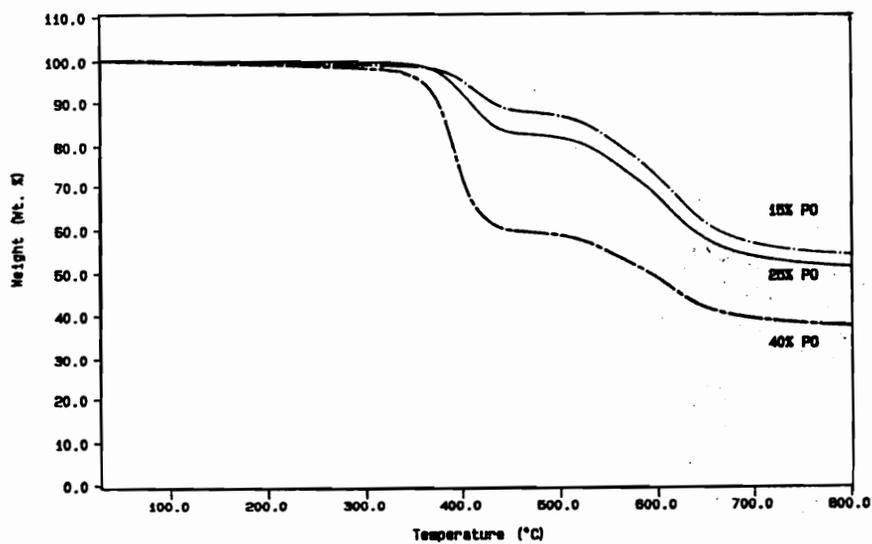
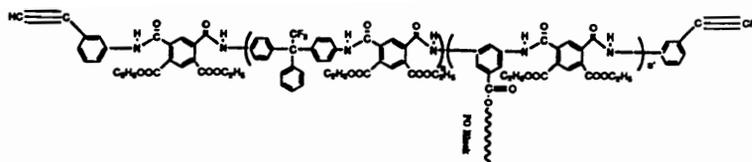


Figure 4.3.4.15 Dynamic TGA of the Crosslinked Polyimide-Poly(propylene oxide) Copolymers Obtained From Copolymers 2, 3, and 4.

ester) oligomers. Hence, in generating of graft copolymers the molecular weight of the poly(amic alkyl ester) was also controlled to 3000 g/mole. The graft copolymers were generated using diamino benzoate terminated poly(propylene oxide) macromonomers. The reaction scheme for the synthesis of ethynyl terminated graft poly(amic alkyl ester) copolymers is shown in Figure 4.3.4.13. This procedure involved the incremental addition of a solution of PMDA meta diethyl ester diacyl chloride in THF to an NMP solution of diamine terminated poly(propylene oxide), 3FDA and pyridine. The solids composition was maintained at approximately 15% for each of polymerization. The polymerization was allowed to proceed for at least 12 hours. The copolymers were then isolated in a methanol/water mixture, rinsed with water to remove the remaining salts, rinsed with isopropanol to remove possible poly(propylene oxide) homopolymers, and dried at 50°C for 24 hours under vacuum.

The composition of poly(propylene oxide) in the copolymer was assessed by both ^1H NMR and TGA. Figure 4.3.3.14 shows the ^1H NMR of the poly(amic alkyl ester) copolymer containing 25 wt.% of the poly(propylene oxide) block of molecular weight 3100 g/mole. These results are provided in Table 4.3.3.4. Figure 4.3.4.15 shows the dynamic TGA profile of the imidized copolymer obtained from the meta-poly(amic alkyl ester) Copolymers 2 to 4. In order to make copolymer films from the alkyl ester copolymers, the samples were dissolved in NMP, cast and cured up to 300°C for 3 hours. The temperature was increased directly to 300°C, at a rate of 20°C/min, in order to obtain good free standing films.

Dynamic mechanical results of the polyimide-poly(propylene oxide) graft copolymers, obtained from poly(amic alkyl ester) copolymers, were similar to those of the polyimide-poly(propylene oxide) copolymers. These materials also exhibited two transitions: a low temperature transition occurring at around -60°C, corresponding to that of the poly(propylene oxide); and a high temperature transition, corresponding to that of the

polyimide block. Figure 4.3.4.16 shows the dynamic mechanical spectrum for Copolymers 2-4. It was clearly demonstrated that as the poly(propylene oxide) wt.% is increased from 14 to 40 %, the low temperature transition peak becomes more and more prominent and less broad, indicating sharper phase separation and lower interfacial mixing. However, with higher wt.% of the poly(propylene oxide), the material is observed to become softer as the temperature is increased. The higher temperature transition was observed to be independent of the wt.% of the poly(propylene oxide) in the material. This is expected to correspond to the degradation temperature of the poly(propylene oxide) block, resulting in a lowering of modulus and an increase of the tan δ peak. The glass transition of the polyimide was observed to be higher than 450°C.

In order to develop foams from these materials, the samples were heated in air at 270°C for 10 hours. The density of the foamed films was measured and is provided in Table 4.3.4.5.

Table 4.3.4.5 Characteristics of PMDA/3FDA/Polyimide Foams From Poly(amic alkyl ester) Copolymers.

Sample	Composition (wt%)	Density (g/cm ³)	Volume Fraction of Voids (%)
1	19	1.15	14
2	14	1.18	11
3	19.5	1.13	16
4	38.5	1.01	25

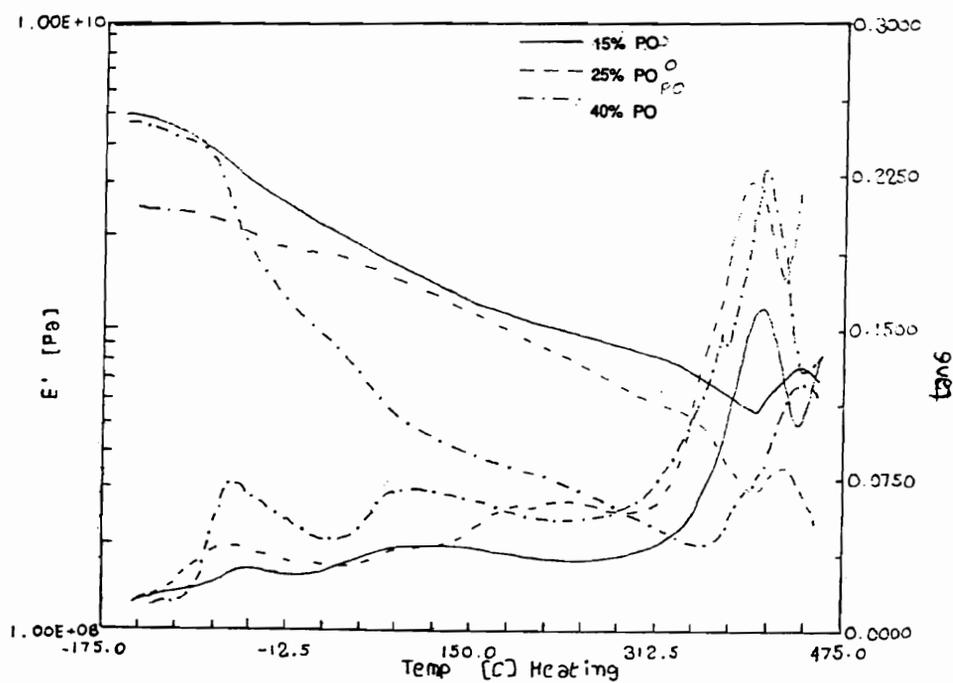
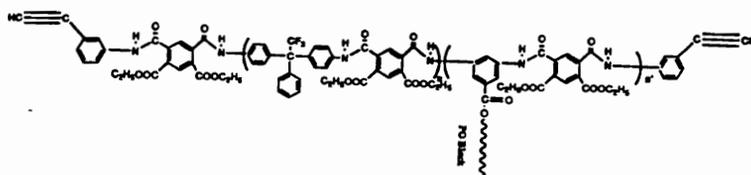


Figure 4.3.4.16 Dynamic Mechanical Spectrum of Crosslinked Polyimide-Poly(propylene oxide) Copolymer Obtained From Copolymer 2 to 4

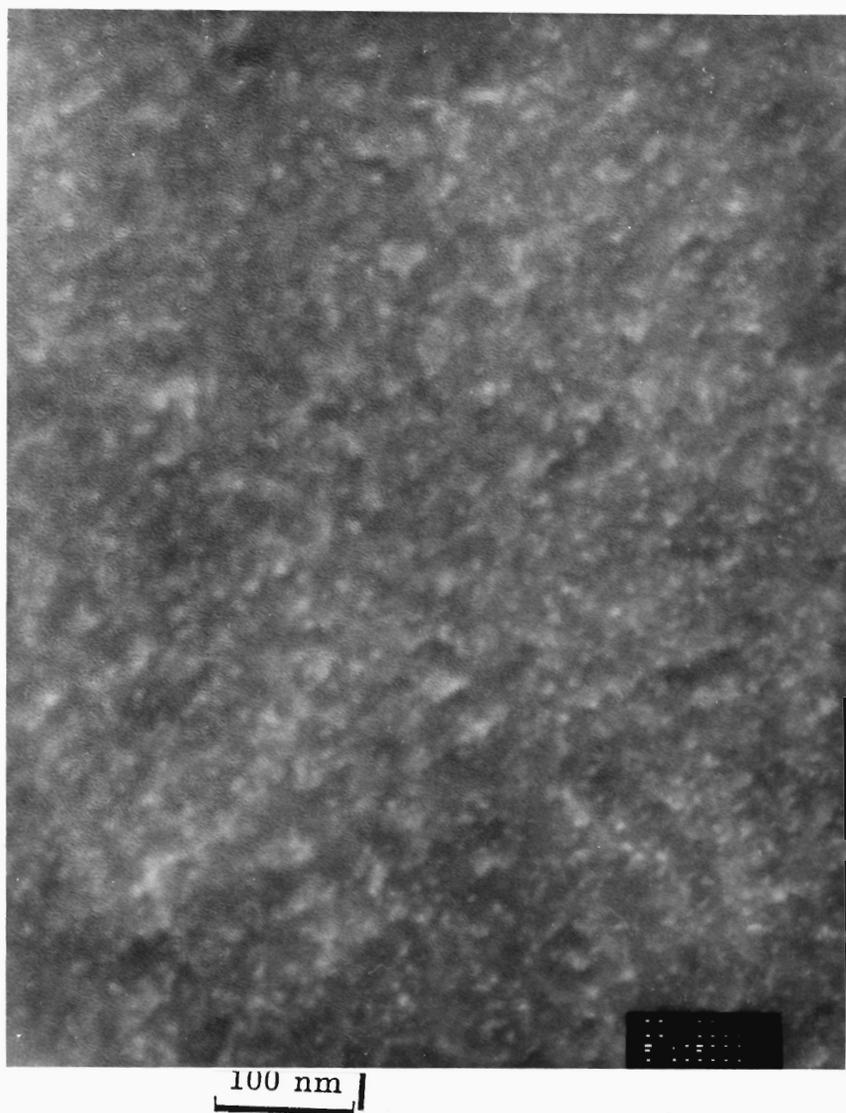


Figure 4.3.4.17 Electron Micrograph of Crosslinked Polyimide Nanofoam from Copolymers 1(187, 000 X).

The density of the films clearly shows the development of the porosity. From these values it is evident that a considerable amount of foam collapse began to occur when the wt.% of the poly(propylene oxide) was increased above 25 wt.%. The foaming efficiency for these materials was observed to be poor, especially at higher wt.% of the poly(propylene oxide) compositions. The foam collapse could be attributed to two factors a) poor crosslinking efficiency whereby by-products plasticize the matrix heavily causing the foams to collapse, or b) an increase in the sample stress due to further crosslinking as the materials are foamed, thus causing the foams to collapse. TEM was performed on the polyimide - propylene oxide graft copolymers obtained from the crosslinked poly(amic alkyl ester)s copolymers after the decomposition of the propylene oxide block. The TEM for foamed Copolymer 1 is provided in Figure 4.3.4.17. The dark regions in the micrograph correspond to the polyimide matrix. From the micrograph, it is evident that a porous structure was obtained. It is also clear that discrete pores with very little to no interconnectivity between the pores had been achieved, as with the uncrosslinked graft copolymers. The pore size was also observed to be in the same range for foams obtained from uncrosslinked graft copolymers.

The cellular structure of the foams were also confirmed using SAXS. The SAXS profile for the unfoamed Copolymer 1, as well as the same foamed polyimide film, exhibited a well defined peak . The plot of intensity as a function of the scattering vector is shown in Figure 4.3.4.18 for copolymer 1 and 4. Presence of the sharp peak seen in the unfoamed film also verifies the presence of phase separated morphology as observed using DMTA. It also demonstrates that the dispersed poly(propylene oxide) phase has some ordering in the polyimide matrix. Once again on foaming the intensity of the SAXS peak was again observed to greatly increase, strongly supporting the formation of pores in the polyimide matrix.

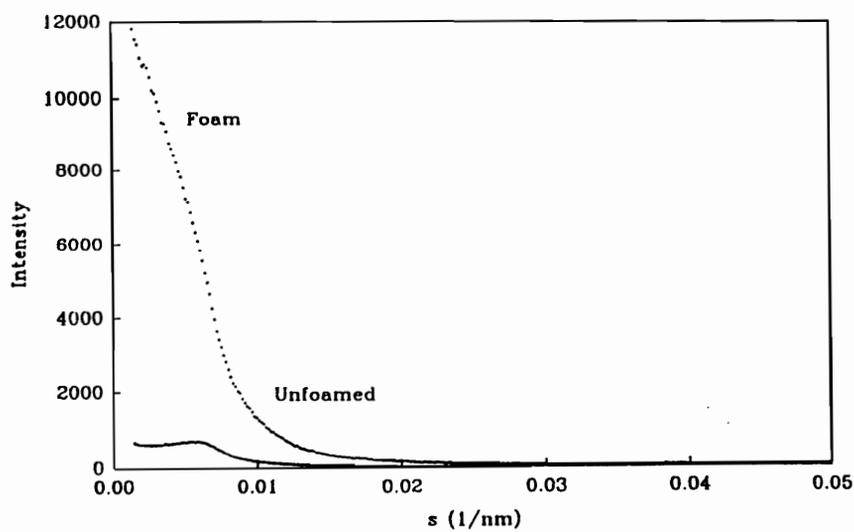
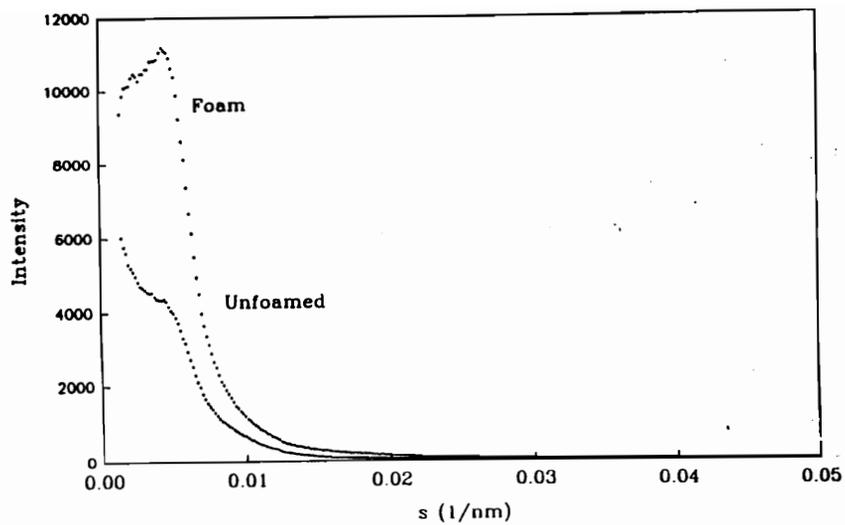


Figure 4.3.4.18 The Plot of Intensity as a Function of the Scattering Vector are Shown in for a) Copolymer 1 and b) for Copolymer 4.

Thin film coating of crosslinked Copolymers 1 to 4 was attempted on a silicon wafer to perform stress and refractive index measurements. While curing these samples, obvious cracks appeared, resulting in very poor films. Such results were not observed for thicker films. This can be attributed to the low solvent in thinner films, which are manifested in very low polymer plasticization rates, providing insufficient mobility for the chain extension to occur. Thus ethynyl endcapped systems failed to produce stable foams as did of the uncrosslinked material.

In the case of block copolymers, mono amine terminated poly(propylene oxide) of molecular weight 5600 g/ mole was used, while three different ethynyl compositions 5, 25 and 35 mole % was attempted. The ethynyl composition was varied by controlling the amount of comonomer 3EDA added to the reaction. The propylene oxide compositions was varied from 15 to 35 wt. %. The reaction scheme for the synthesis of ethynyl terminated graft poly(amic alkyl ester) copolymers are shown in Figure 4.3.4.19. The synthesis involved the incremental addition of a solution of PMDA meta diethyl ester diacyl chloride in THF to an NMP solution of diamine terminated poly(propylene oxide), 3FDA, pyridine and various amounts of comonomer EDA. The solids composition were maintained at approximately 15% for each of polymerization. The polymerization was allowed to proceed for at least 12 hours. The copolymers were isolated in a methanol/water mixture, rinsed with water to remove the remaining salts, rinsed with isopropanol to remove possible poly(propylene oxide) homopolymers, and dried at 50°C for 24 hours under vacuum.

The compositions of poly(propylene oxide) in the copolymer was assessed by both ^1H NMR and TGA and are provided in Table 4.3.4.6. In order to produce copolymer films from the alkyl ester copolymers, the samples were dissolved in NMP, cast and cured up to 300°C for 3 hours. The temperature was increased directly to 300°C at 20°C/min in order to obtain good free standing films.

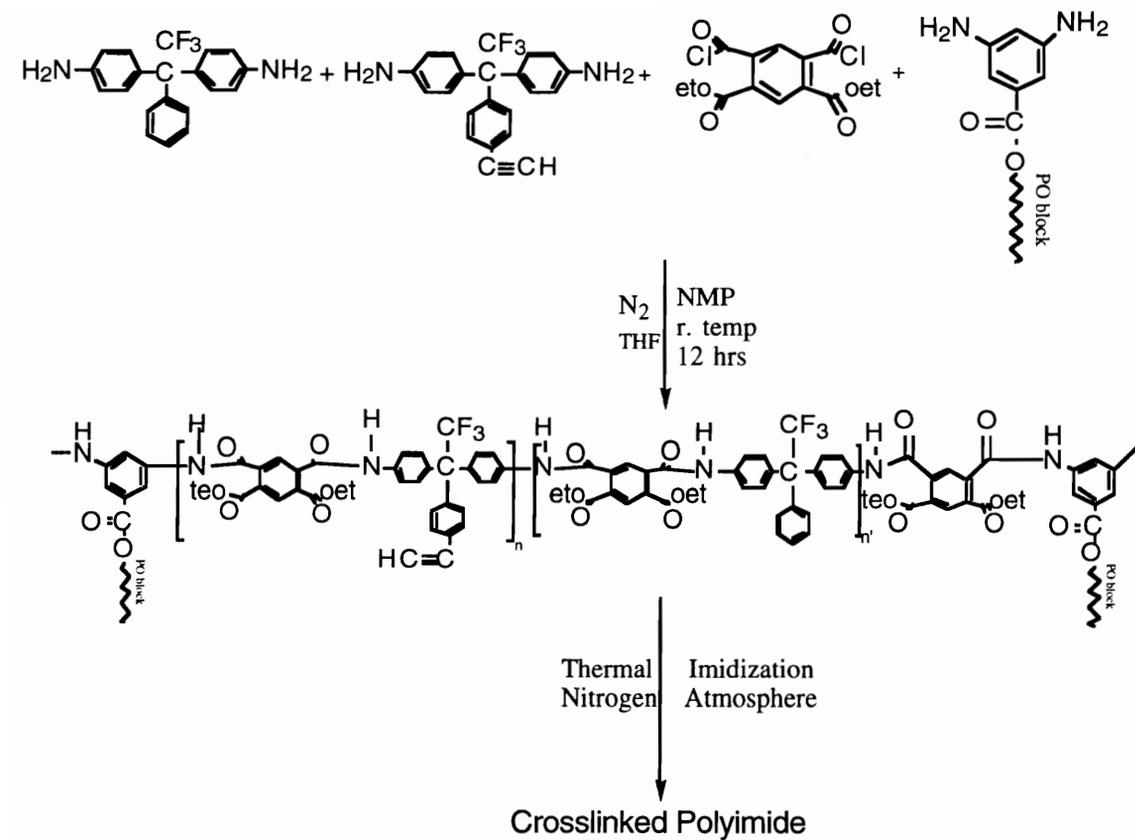


Figure 4.3.4.19 Synthesis of Pendant Ethynyl Containing PMDA/3FDA/Poly(propylene oxide) Block Copolymers (poly(propylene oxide) block length 5600 g/mole)

Table 4.3.3.6 Characteristics of meta-Poly(amic alkyl ester) of PMDA/3FDA
/Poly(propylene oxide) Copolymers Containing Pendant Ethynyl Groups.

Sample	Ethynyl Composition, Mol % of EDA, added	Propylene Oxide Charged	Wt. % of Propylene oxide incorporated		Volume Fraction of Propylene oxide, %
			TGA	¹ H NMR	
1	5	25	17	15.7	19
2	25	15	15	13	17
3	25	25	-	23.5	28
4	25	35	36	34	42
5	40	25	26	26	31
6	40	35	38	37	44

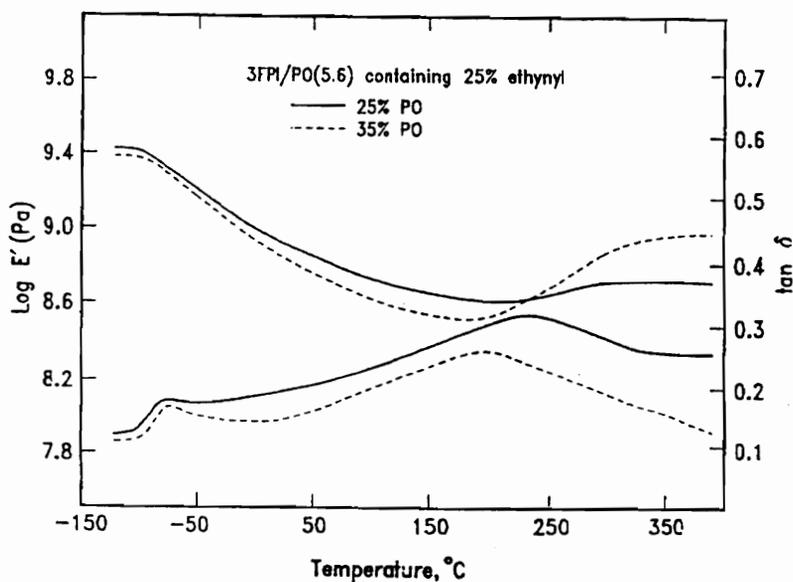
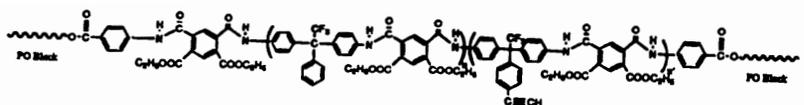


Figure 4.3.4.20 Dynamic Mechanical Spectrum of Crosslinked PMDA/3FDA/Polyimide-Poly(propylene oxide) Copolymer 3 and 4 from Pendant Ethynyl Containing Poly(amic alkyl ester) Copolymers.

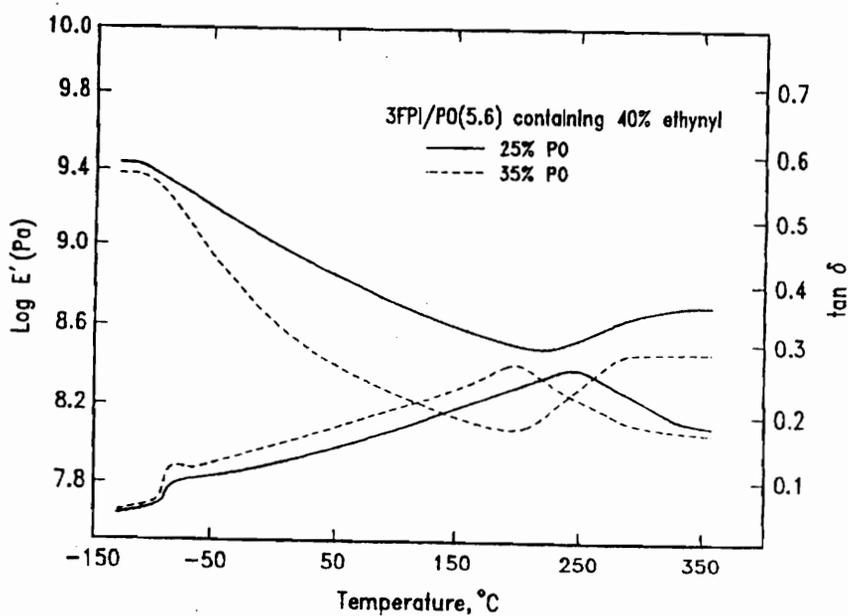
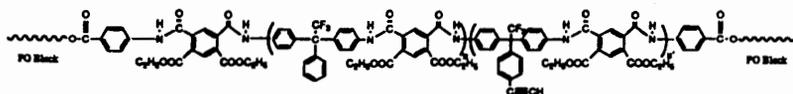


Figure 4.3.4.21 Dynamic Mechanical Spectrum of Crosslinked PMDA/3FDA/Polyimide-Poly(propylene oxide) Copolymer 5 and 6 from Pendant Ethynyl Containing Poly(amic alkyl ester) Copolymers.

Dynamic mechanical results of the polyimide-poly(propylene oxide) graft copolymers obtained from poly(amic alkyl ester) copolymers were similar to those of polyimide-poly(propylene oxide) copolymers. These materials also exhibited two transitions: a low temperature transition occurring at approximately -60°C , corresponding to that of the poly(propylene oxide), and a high temperature transition corresponding to that of the polyimide block. Figure 4.3.4.20 shows the dynamic mechanical spectrum for Copolymers 3 and 4, while Figure 4.3.4.21 shows the dynamic mechanical spectrum for Copolymers 5 and 6.

In order to develop foams from these materials, the samples were heated in air at 270°C for 10 hours. The density of the foamed films was measured and is provided in Table 4.3.4.7. The density of the films clearly show the development of the porosity. From the density values that not much collapse of the foam occurred when the wt.% of the poly(propylene oxide) was increased. The foaming efficiency for these materials were observed to go up with respect to higher crosslink density. Furthermore, the foams efficiency was greater for these materials than observed for the uncrosslinked materials. Transmission electron microscopy was performed on these materials. No difference in pore shape or size was observed for the foamed crosslinked materials obtained from copolymers containing lower percentage of poly(propylene oxide) i.e. $<25\%$, while the shape of the pores dramatically changed for foams obtained from copolymers containing $>25\%$ of poly(propylene oxide). Figure 4.3.4.22 shows the electron micrograph for foam obtained from Copolymer 6. The darker regions of the micrograph correspond to the polyimide matrix. These results suggest that on degradation of the propylene oxide, the degradative products tend to behave more like blowing agents creating much larger pores than the ones observed in the uncrosslinked graft or block copolymers. Also, the pores were noted to be highly interconnected in nature.

Table 4.3.4.7 Characteristics of Crosslinked PMDA/3FDA/Polyimide Foams from Pendant Ethynyl Containing Poly(amic alkyl ester) Copolymers.

Sample	Ethynyl Composition, Mol % of EDA	Propylene Oxide composition, wt%, From ¹ H NMR	Density g / cm ³	Volume Fraction of Voids (%)
1	5	15.7	1.03	23
2	25	13		-
3	25	23.5	0.97	49
4	25	34	0.59	56
5	40	26	0.53	60
6	40	37	0.51	62



Figure 4.3.4.22 Electron Micrograph of Crosslinked PMDA/3FDA/Polyimide-Poly(propylene oxide) Foam from Pendant Ethynyl Containing Poly(amic alkyl ester) Copolymers 6. (187,000 X)

Thus, these results suggest that stable foams with better foaming efficiencies can be obtained via crosslinking chemistry. These results also suggest that crosslinking schemes for generating stable foams are best designed around pendant ethynyl functionalized materials, rather than end functionalized materials. The low molecular weights of the end functionalized materials coupled with less efficient crosslinking, tends to provide very poor thin films. With regards to the pendant functionalized materials, more efficient crosslinking can be obtained by varying the amount of the comonomer incorporated in the polymer chain. Also the molecular weights are much larger than those seen in the end functionalized systems, and thus can provide better and more uniform thin film coatings. These results also support the hypothesis that pendant or end functionalized ethynyl crosslinking chemistry, used in conjunction with poly(amic alkyl ester) precursor provided higher and better crosslinked materials than via the fully cyclized ethynyl end functionalized materials. Crosslinked materials also to afford solvent resistant materials with higher foaming efficiency.

4.3.5. Synthesis and characterization of polyimide copolymers for foams from PMDA/3FDA based polyimide-poly(ethylene oxide) graft copolymers

In the previous three sections polyimide foams have been successfully developed using polyimide as the thermally stable block and poly(propylene oxide) as the thermally labile block. Poly(propylene oxide) had worked out well for the foam generation because it is stable at temperatures as high as 300°C in an inert atmosphere, allowing solvent removal and imidization, if necessary. However, when exposed to oxygen, the decomposition temperature drops dramatically ($\approx 200^\circ\text{C}$) such that temperatures well below T_g of many polyimides can be used to facilitate the foaming process. The degradation of poly(propylene oxide) is clean and the by-products of the degradation are environmentally friendly. But there are some inherent problems with the use of poly(propylene oxide). The mono-hydroxy poly(propylene oxide) is not commercially available in bulk quantities and this hinders the large scale synthesis and analysis of this foaming process. Also mono-hydroxy poly(propylene oxide) are usually synthesized via the anionic ring opening polymerization of propylene oxide monomer at about 80°C. This leads to side reactions as shown in Figure 4.3.5.1. Side reactions generate a considerable amount of allyl groups, which may or may not isomerize into propylene groups. These side reactions prevent the formation of very high molecular weight poly(propylene oxides) via the anionic technique. These reactions also help in reducing the thermal stability of the poly(propylene oxide).

In order to generate foams containing large pores, higher molecular weight poly(propylene oxide) was required. However, the unavailability of high molecular weight poly(propylene oxide), coupled with its commercial absence in the mono hydroxy form in large amounts, prompted us to investigate other materials as labile groups.

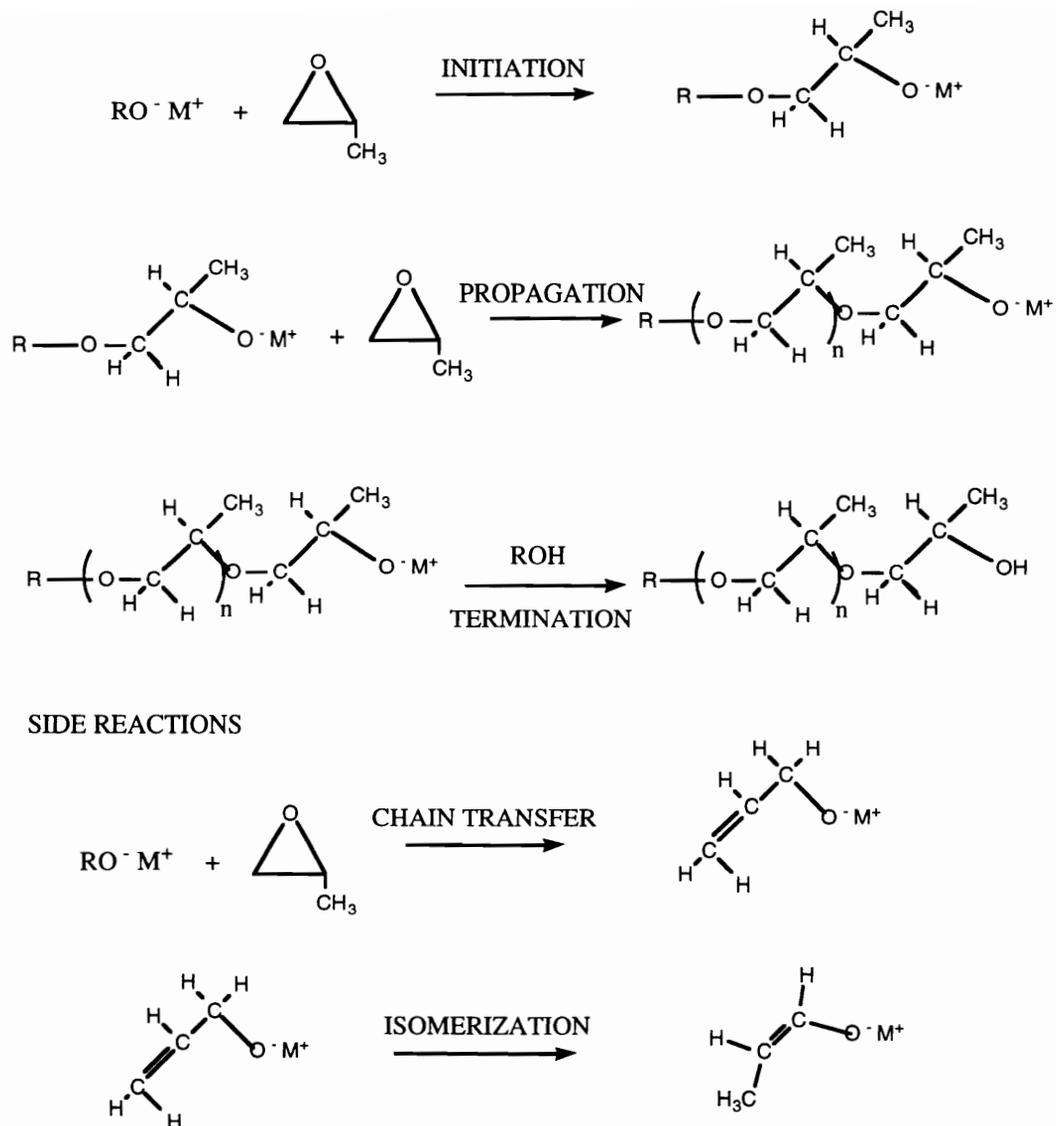


Figure 4.3.5.1 Mechanism and Side Reactions of Anionic Polymerization of Propylene Oxide

One material that has almost the same chemical structure and similar thermal stability to the poly(propylene oxides) are the poly(ethylene oxides)(PEO). PEO's are cheap materials, commercially available in wide range of molecular weights, and are available the mono-hydroxy form. Being highly crystalline in nature, the PEO's are expected to phase separate similar, or even more efficiently than the poly(propylene oxides) with polyimide matrix. Mono hydroxy terminated high molecular materials of poly(ethylene oxide) can also be easily synthesized when necessary. Madorsky and Straus have compared the kinetics of thermal degradation of poly(ethylene oxide) and poly(propylene oxide). They determined that the poly(ethylene oxide)s are slightly more stable than poly(propylene oxide), and that the thermal degradation rates of poly(propylene oxide) is a little higher than that observed for poly(ethylene oxide). Mass spectral analysis of the by-products of degradation has resulted in very similar degradative products. Thus, these encouraging results prompted us to investigate the thermal degradation profiles of poly(ethylene oxide) in air and nitrogen.

In order to evaluate the thermal stability of poly(ethylene oxide), commercially available mono-hydroxy poly(ethylene oxide) of molecular weight 5000 g/mole was heated in both air and nitrogen atmosphere. Figure 4.3.5.2 shows the TGA profile of PEO in air and nitrogen atmosphere. As expected, these materials were observed to be stable in nitrogen well above 300°C, while in air they began to degrade at 230°C and above. Like poly(propylene oxide), poly(ethylene oxide) is expected to generate foams because it is stable at temperatures as high as 300°C in an inert atmosphere, allowing solvent removal and imidization, if necessary. However, when exposed to oxygen, the decomposition temperature drops dramatically ($\approx 230^\circ\text{C}$) such that temperatures well below T_g of many polyimides facilitate the foaming process. For successful foam generation, polyimide-poly(ethylene oxide) copolymers were synthesized. This required the synthesis of diamine

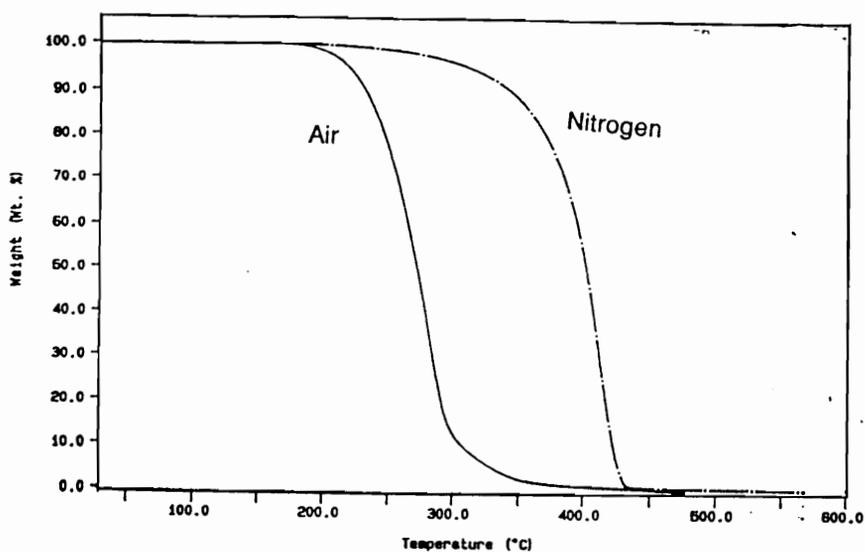
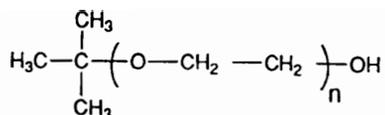


Figure 4.3.5.2 TGA Thermogram of mono-Hydroxy Poly(ethylene oxide) of Molecular Weight 5000 g/mole in Air and Nitrogen

terminated poly(ethylene oxide) blocks in order to incorporate PEO successfully into the polyimide matrix.

Monohydroxy PEO of molecular weight 5000 g/mole was derivatized into diamino benzoate terminated oligomers amenable towards polyimide copolymerization via the same two step process described for the poly(propylene oxide). Monohydroxy terminated PEO oligomer was reacted with 3,5 dinitrobenzoyl chloride in a dry tetrahydrofuran solvent containing pyridine as the acid acceptor at 60°C. After the reaction the solution was filtered to remove pyridine hydrochloride salt, and the filtrate was further rotovaped to remove the solvent resulting in a clear solid dinitro terminated poly(propylene oxide) oligomer. The dinitro terminated PEO was later recrystallized from acetone three times to obtain pure dinitro terminated PEO. The dinitro terminated poly(propylene oxide) was characterized using ¹H NMR to conform complete conversion of the hydroxy group to the dinitro benzoate functionalized PEO. It was then hydrogenated with Pearlman's catalyst (palladium hydroxide on carbon) and hydrogen in tetrahydrofuran to the respective diamino benzoate functionality. The molecular weights of the amino benzoate functionalized PEO was characterized using both ¹H NMR and standard potentiometric titration of the amine end groups against standardized solution of HBr in acetic acid. This results is shown in Table 4.3.5.1.

Table 4.3.2.1 Characterization of Diamino Benzoate Terminated PEO Oligomers

Sample	Molecular Weights (g/ mole)		
	Target	¹ H NMR ³	From Titration's ⁴
1	5000	5750	5300

³based on diamine terminated PO; ⁴amine end groups titrated against HBr/AcOH mixture

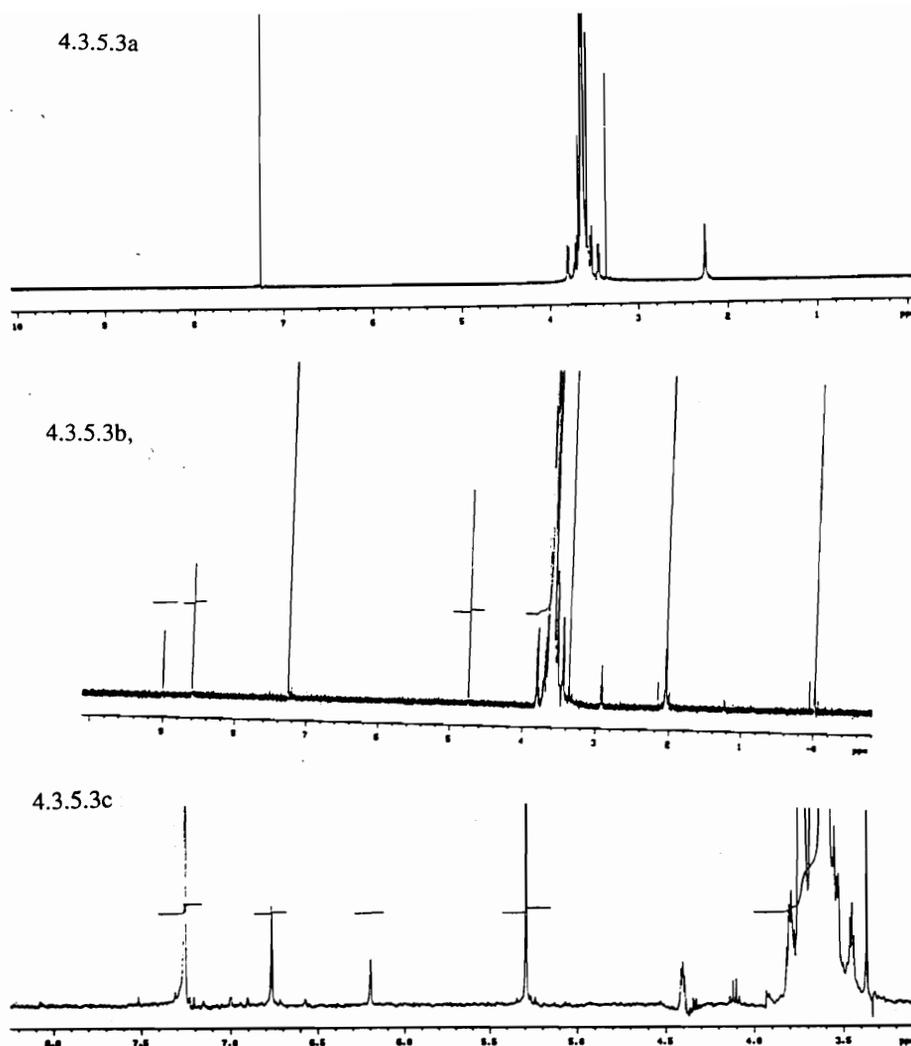


Figure 4.3.5.3 ^1H NMR of the PEO (mol wt = 5300 g/mole) Oligomer Functionalized with Monohydroxy, Dinitro and with Diamine Functional Groups are shown in Figure 4.3.5.3a 4.3.5.3b, and 4.3.5.3c respectively

^1H NMR of the PEO (mol wt = 5300 g/mole) oligomer functionalized with monohydroxy, dinitro and with diamine functional groups are shown in Figure 4.3.5.3a, 4.3.5.3b, and 4.3.5.3c, respectively. Potentiometric titration profile of the amine functionalized PEO (mol.wt = 5300 g / mole) is shown in Figure 4.3.5.4.

The copolymer synthesis involved the addition of the solid PMDA to a solution of 3FDA and the diamine functionalized PEO oligomer, as described in the synthesis of poly(propylene oxide) copolymers. The reaction scheme for the synthesis of the copolymer is provided in Figure 4.3.5.5. The polymerization's were carried out in NMP at solid compositions of approximately 15 wt%. The polymerization's were maintained at ambient temperature for 24 hours yielding viscous solutions of the target poly(amic acid). Imidization of the poly(amic acid) solutions was carried out directly, which was accomplished by adding in excess acetic anhydride and pyridine in 6 - 8 hours at 80°C. The use of the diamine terminated PEO oligomers afforded a graft copolymer, where the PEO has been grafted on the polyimide main chain.

In order to test the viability of producing foams from PEO copolymers, one imide - PEO copolymer was prepared. The PEO oligomer with a composition of 25 wt% was investigated and these result are provided in Table 4.3.5.2. Presence of any unreacted PEO oligomers was completely removed by stirring the precipitated copolymer overnight in hot methanol. The composition of the PEO in the copolymer was assessed by both ^1H -NMR, by comparing the integrated aromatic protons of the polyimide to those of the aliphatic protons of the ethylene oxide, as shown in Figure 4.3.5.6; and via TGA, by measuring the weight retention after decomposition of the thermally labile block, as shown in Figure 4.3.5.7. The composition of PEO incorporation into the copolymer was comparable to that initially charged as shown also in Table 4.3.5.2.

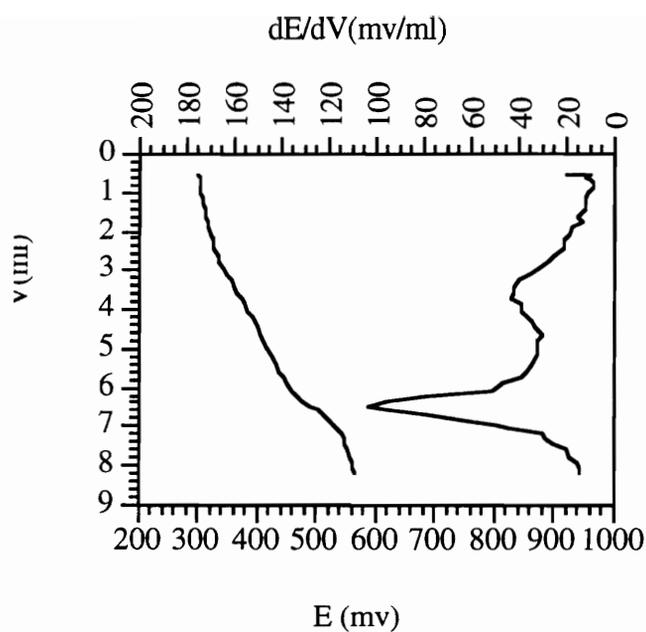


Figure 4.3.5.4 Potentiometric Titration Profile of the Amine Functionalized PEO(mol.wt = 5000 g / mole)

Table 4.3.5.2 Characteristics of PMDA/3FDA/Polyimide-Poly(ethylene oxide) Copolymer

Sample	Weight % of PEO		
	Theoretical	From ¹ H NMR	From TGA
1	25	29	24

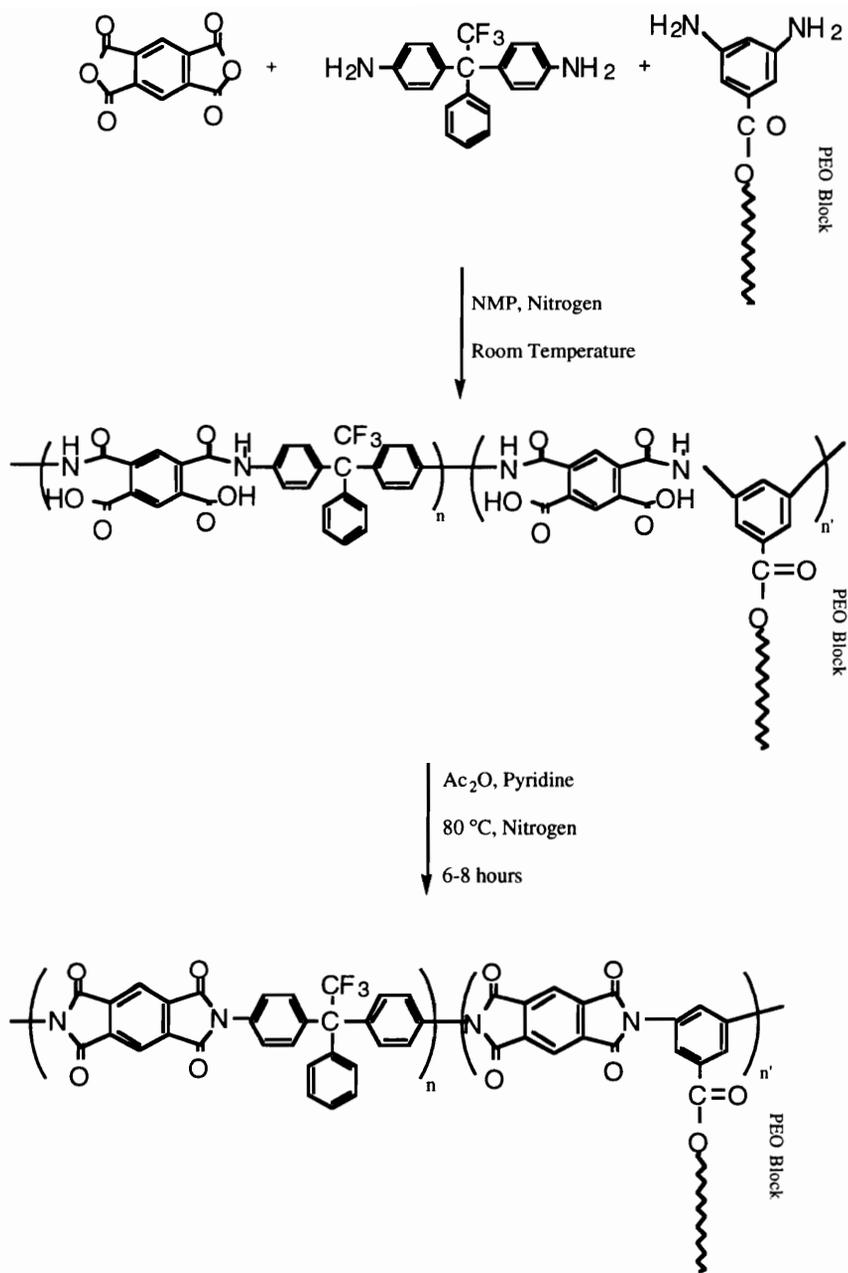


Figure 4.3.5.6 Synthesis of PMDA/3FDA Polyimide-PEO Graft Copolymer

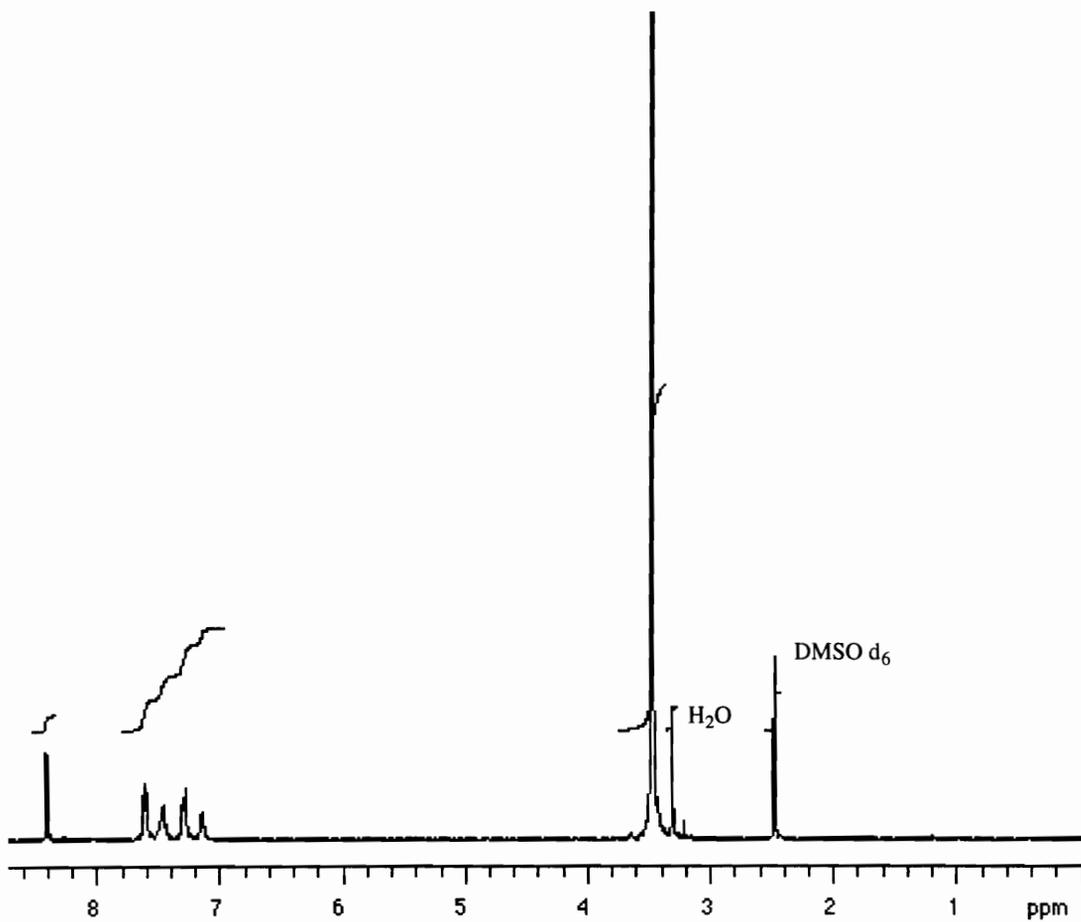
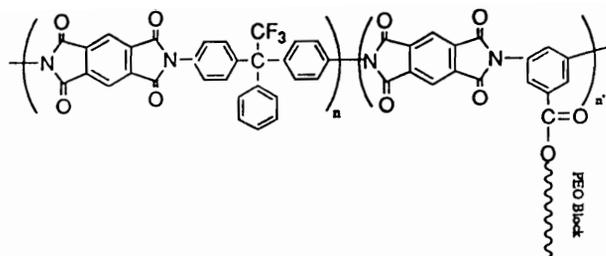


Figure 4.3.5.6 ^1H NMR of PMDA/3FDA Polyimide-PEO Graft Copolymer

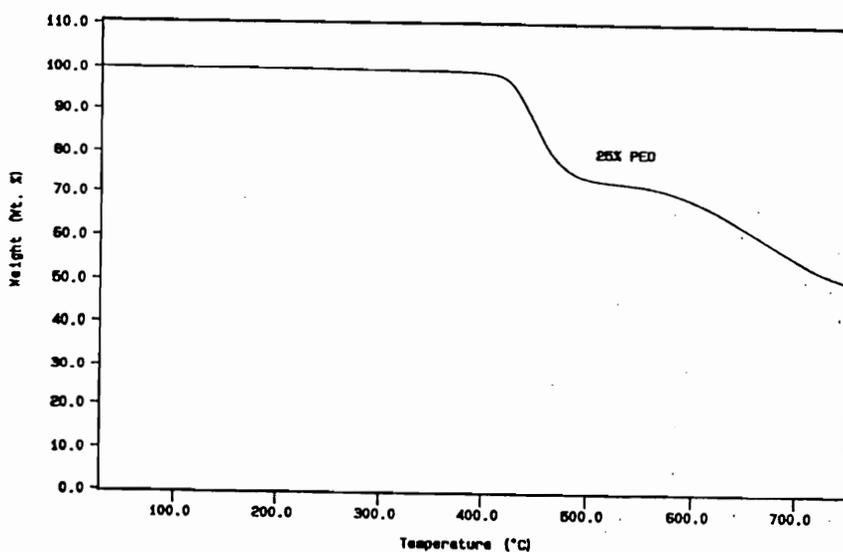
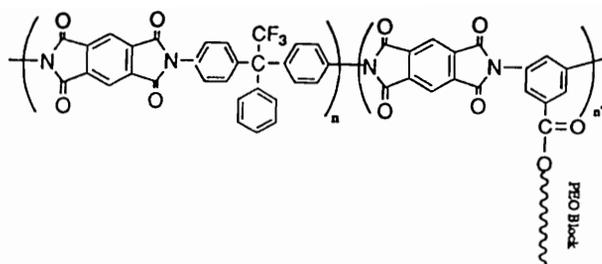


Figure 4.3.5.7 Thermogravimetric Analysis of PMDA/3FDA Polyimide-PEO Graft Copolymer Containing 25 wt.% of the Labile Block

The processing window for film formation was established for 3FDA / PMDA / PEO copolymers using ^1H NMR, TGA and dynamic mechanical measurements. In order to prepare polyimide film samples of PMDA / 3FDA / PO, copolymers were dissolved in NMP and cast on to a glass plate. The glass plate was gradually heated at a rate of $5^\circ\text{C} / \text{min}$ to 300°C and held there for 1 hour under nitrogen atmosphere. This resulted in a slightly hazy, tough polyimide-PEO copolymer film. The ^1H NMR spectra of the samples cured at 300°C showed no detectable traces of the solvent (NMP). Furthermore, integration of the aromatic protons of the polyimide against the aliphatic protons of the ethylene oxide indicated no detectable loss of the thermally labile PEO under these conditions. It was clearly observed that complete removal of the solvent NMP was achieved with minimal loss of PEO.

Dynamic mechanical analysis of the imide - PEO graft copolymers was performed. The copolymer exhibited two transitions characteristic of a microphase separated morphology. The low temperature transition of the PEO phase occurring near -7°C and a higher temperature transition corresponding to that of the polyimide block occurring near 377°C . It is interesting to note that the low temperature transition of the PEO had moved considerably higher than the reported glass transition temperature of -50°C . Conversely, the higher temperature transition of the polyimide was also observed to drop in temperature from the anticipated glass transition temperature of 430 to 377°C . These result indicate a significant amount of interfacial mixing between the polyimide phase and the poly(ethylene oxide) phase. This is the first known report of a polyimide-PEO partially miscible copolymer. This result is provided in Figure 4.3.5.8.

Having demonstrated that the polyimide and PEO are partially miscible, an attempt was give made to obtain foams from these materials. Isothermal TGA experiments in air were performed in order to define the foaming temperatures, for these copolymers. Based

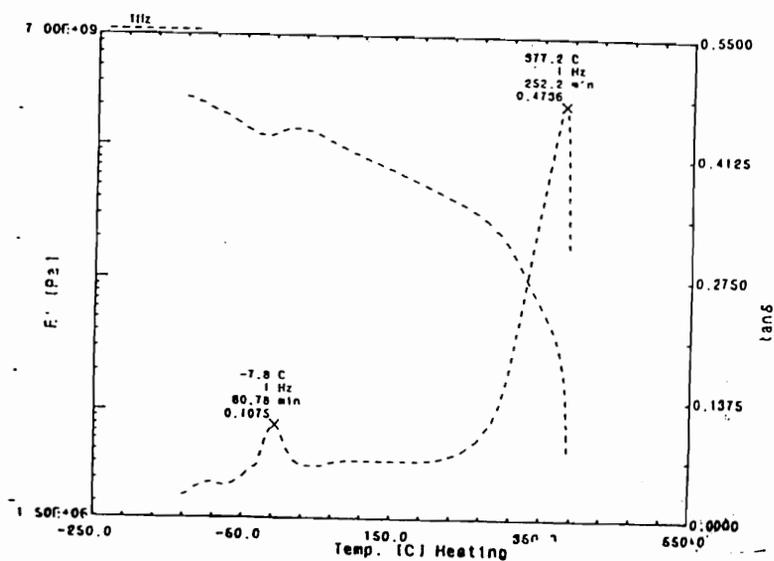
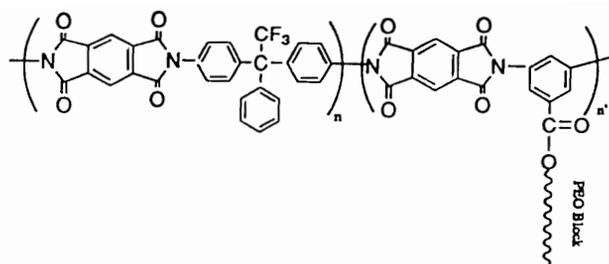


Figure 4.3.5.8 Dynamic Mechanical Spectrum of PMDA/3FDA Polyimide-PEO Graft Copolymer. PEO mol. wt. = 5000 g/ mole, wt. % of labile block = 25%.

on the results obtained from the block copolymers, isothermal experiments were performed at 270 and 300°C. The copolymers exhibited near quantitative decomposition of the PEO component under isothermal TGA experiment in air at 300°C. Based on these isothermal experiments, the foaming temperature for the copolymers was determined as 300°C. Figure 4.3.5.9 plots the isothermal weight loss as a function of time for the PEO copolymers at 270 and 300°C, respectively.

In order to foam the copolymer, films of the copolymer were subjected to the preassigned temperature of 300°C in air for a period of 10 hours. At the end of the foaming process, part of the foamed sample was tested by and thermogravimetric analysis was performed up to 800°C. The TGA spectrum clearly indicated quantitative removal of the PEO coblock as shown in Figure 4.3.5.10.

Density measurements was obtained the foamed polyimide copolymer and compared to those of the homopolymer. These results indicated that the foamed copolymer had the same density as the homopolymer, which signals the complete collapse of the foam occurring on degradation of the PEO component. Transmission microscopy verified the absence of foam formation consistent with the density measurements. A possible reason for the foam collapse is due to the miscible nature of the PEO with the polyimide matrix. Dynamic analysis of the polyimide-PEO copolymer clearly indicated partial miscibility between the two components resulting in the suppression of the polyimides glass transition temperature. This depression in T_g of the imide phase can provide requisite mobility at the experimental foaming temperature of 300°C, thus causing collapse of the voids. This, coupled with the polar degradative by-products from the PEO degradation such as formaldehyde's, ketones, esters and alcohol's, could result in sufficient plasticization of the polyimide matrix causing complete collapse of foam.

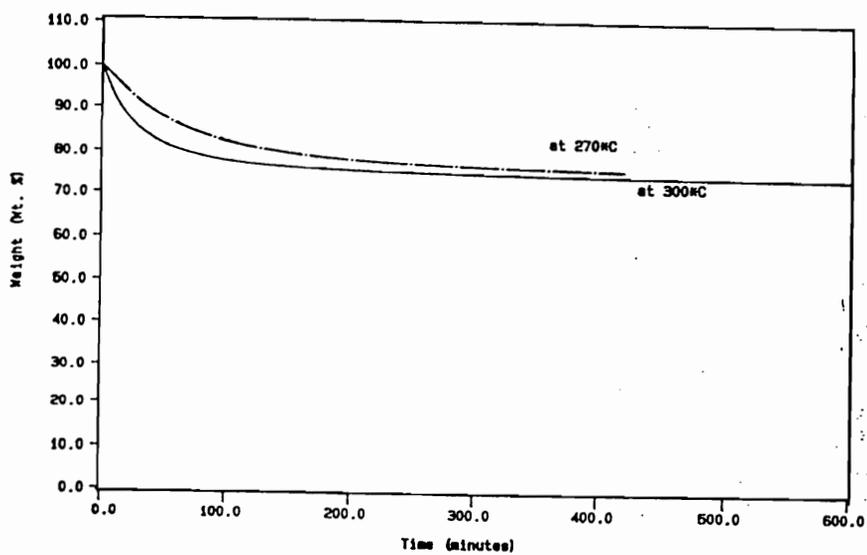
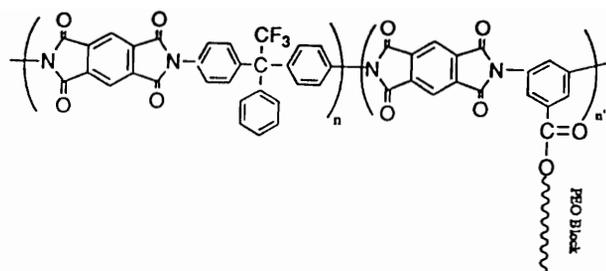


Figure 4.3.5.9 Isothermal TGA of PMDA/3FDA Polyimide-PEO Copolymer Performed in Air at 270 and 300°C.

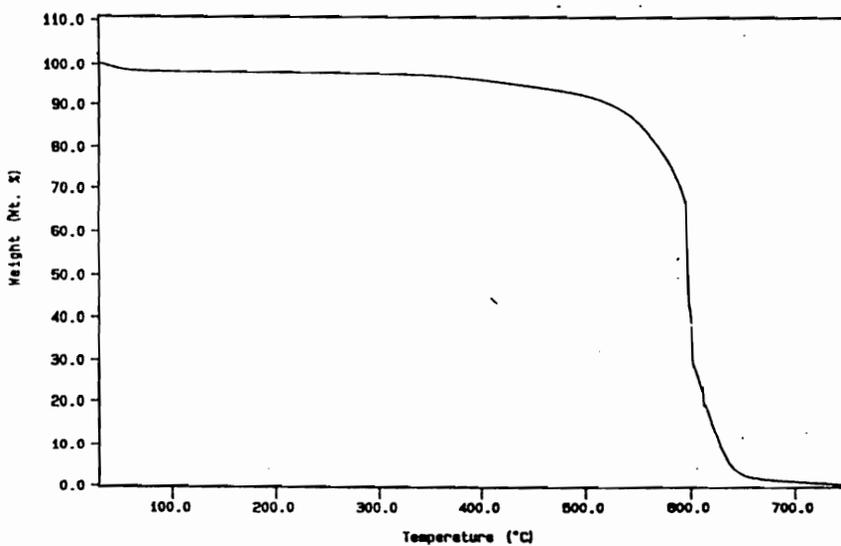
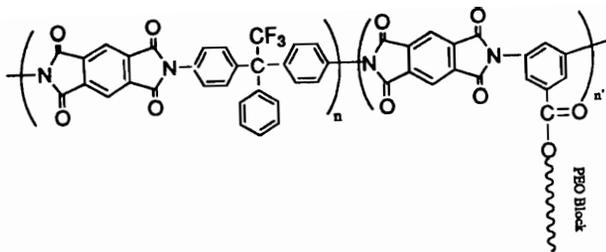


Figure 4.3.5.10 Dynamic TGA Spectrum of PMDA/3FDA Polyimide-PEO Copolymer after the Removal of the Thermally Labile PEO block

4.3.6. Synthesis and characterization of polyimide copolymers for foams from PMDA/3FDA based polyimide-poly(methyl methacrylate) copolymers and blends

It is well known that poly(methyl methacrylate) undergoes depolymerization on heating via an unzipping mechanism and degrades mainly back to monomer units.²⁰⁷ This depolymerization is expected to begin at the ceiling temperature of the polymer. Hence, it was believed that by degrading poly(methyl methacrylate), the resulting monomers could be used as agents for the foaming process. It should be noted that the decomposition temperature of PMMA is strongly dependent on the termination mechanism of the polymerization; i.e., combination or disproportion. Termination by disproportion leads to a substantially lower decomposition temperature. This, in turn, is dependent on the synthetic route employed.²⁰⁸

The use of PMMA as the labile block in the generation of foam requires well defined amine functionalized PMMA oligomers that are viable in standard polyimide synthesis. It is understood that controlled of molecular weight and end group functionality can be achieved using both anionic and group transfer polymerization's. In this study, PMMA of different molecular weights were synthesized using group transfer polymerization technique. In order to generate PMMA-polyimide graft copolymers, diamine functionalized PMMA was necessary. In order to prepare diamine functionalized material, initially mono hydroxy terminated PMMA was synthesized. This was synthesized using a protected hydroxy functionalized initiator route based on 2-hydroxyethyl methacrylate. The hydroxy group of the 2-hydroxyethyl methacrylate was protected using primary hydroxyl group due to the sensitivity of the GTP process to protic sources. The other trimethyl silyl group, which is part of the silyl ketene acetal portion of the molecule, forms the active portion during polymerization.

Upon successful polymerization of the MMA monomer in the presence of the initiator, followed by termination of the MMA polymerization with methanol, the polymer was observed via ^1H NMR to have the protected hydroxyl functionality in the form of the trimethyl silyl ether as the end group. This protecting group was hydrolyzed using dilute solution of HCl in methanol to liberate the primary hydroxyl end group. Using this procedure mono hydroxy functionalized PMMA of 3 different molecular weights (8000 g/mole, 15,000 g/mole and 45,000 g/mole) were synthesized. These reactions were monitored by ^1H NMR, as shown in Figures 4.3.6.1 - 4.3.6.2. Figure 4.3.6.1 represents the spectrum of the 8000 g/mole PMMA macromonomer terminated with the trimethylsilyl end group. The peak at 0.12 ppm is due to the methyl protons of the protective group while the peak at 0.1 represents the trimethylsilyl group of the ketene acetal. The peak at 3.6 ppm corresponds to the methyl groups of the methyl ester of PMMA repeat unit. Figure 4.3.6.2 shows the product of the hydrolysis of the trimethylsilyl protecting group. The disappearance of the peak at 0.1 and 0.12 ppm is evident, indicating complete hydrolysis of the silyl groups.

Since GTP is a living polymerization process, polymers of controlled molecular weight having narrow molecular weight distribution can be synthesized.²⁰⁹ The Figure 4.3.6.3 shows the GPC trace of the synthesized PMMA macromonomers. The peaks are quite narrow, indicative of the near monodisperse nature of the polymers. The molecular weight averages of the macromonomer obtained by GPC are provided in Table 4.3.6.1. The $\langle M_n \rangle$ values were observed to be slightly higher than the target molecular weight in all cases. The polydispersity indices were all very low, ranging from 1.1 to 1.4.

The primary hydroxy functionalized 15,000 g/mole PMMA was converted to dinitro functionalized material by reacting with 3,5-dinitrobenzoyl chloride, in the presence of pyridine as the acid acceptor. Upon completion of the reaction the pyridinium

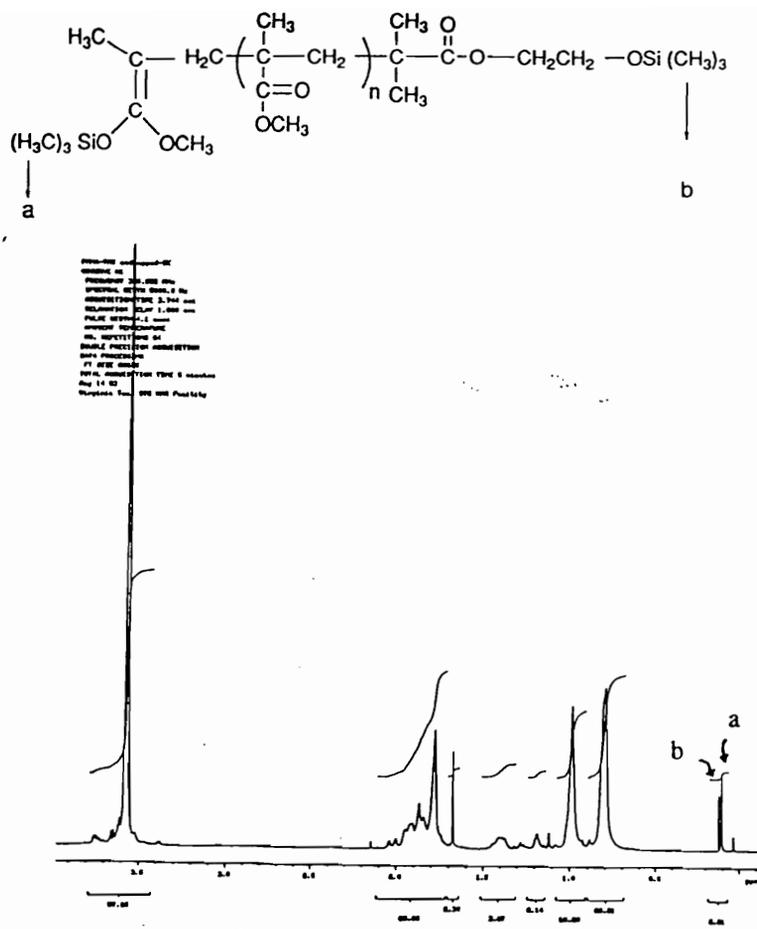


Figure 4.3.6.1 ^1H NMR Spectrum of Trimethyl Silyl Protected Hydroxy Terminated PMMA

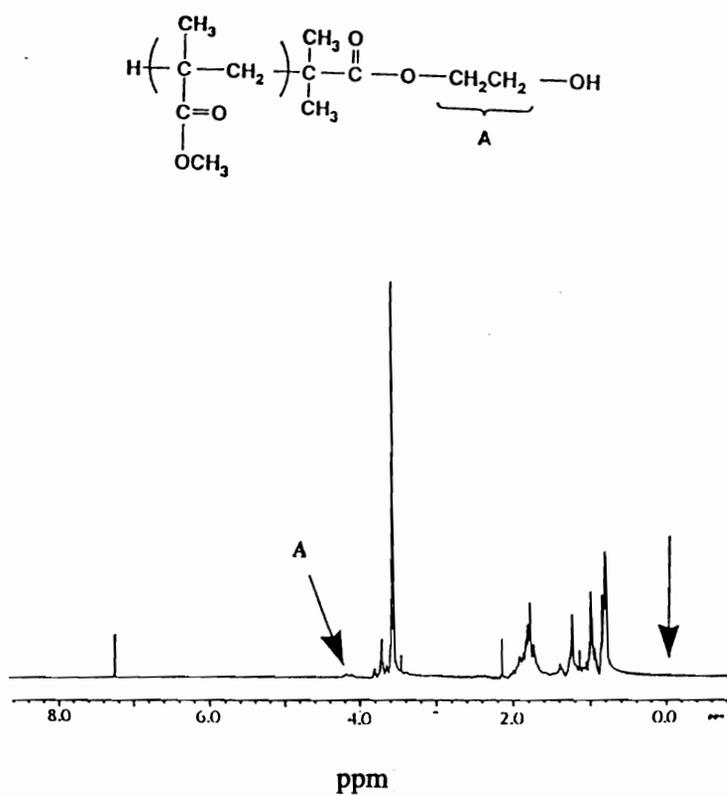


Figure 4.3.6.2 ^1H NMR Spectrum of Hydroxy Terminated PMMA

Table 4.3.6.1 Characteristics of PMMA Macromonomers

Molecular Weight Analysis					Intrinsic Viscosity	T _g (DSC)
Target	From ¹ H NMR	GPC			[dl/g] _{in} THF at 25°C	(°C)
		< Mn >	< Mw >	Polydispersity		
5000	7640	7600	8590	1.13	0.066	108
15000	17550	18220	20470	1.12	0.095	112
45000	-	38750	44160	1.14	1.12	114

hydrochloride salts were filtered over celite and washed with tetrahydrofuran. The polymer was isolated by adding it slowly into a well stirred solution of methanol and water (75/25). The resulting white powder was filtered and dried in a vacuum oven. The dinitro functionality was later reduced to the diamine functionality by reducing the nitro groups to the amino groups using stannous chloride in methylene chloride / methanol mixture (75/25) for 48 hours at about 50°C. Conversion of the hydroxy group to the dinitro groups results in the introduction two new aromatic peaks at 9.05 and 9.1 ppm respectively as shown in Figure 4.3.6.4. The molecular weight of the synthesized polymers was obtained by integration of the aromatic protons with the methyl protons at 3.6 ppm of the PMMA ester. These results are also provided in Table 4.3.6.1. Figure 4.3.6.5 shows the NMR spectrum of the diamine terminated macromonomer. The disappearance of the two aromatic nitro peaks at 9.05 and 9.1 ppm and the appearance of the aromatic protons at 6.2 and 6.8 ppm clearly indicates complete reduction of the nitro groups to the amine functionality.

In order to evaluate the thermal stability of poly(methyl methacrylate), GTP polymerized PMMA of 8000 g/mole was heated in both air and nitrogen atmosphere. Figure 4.3.6.6 shows the TGA profile of PMMA in air and nitrogen atmosphere. As expected, these materials were to be stable in nitrogen well above 325°C, while in air, they began to degrade at 300°C and above. Thus, as in the case of poly(propylene oxide), PMMA is also expected to be effective for foam generation because it is stable at temperatures as high as 325°C in an inert atmosphere, allowing solvent removal and imidization, if necessary. However, when exposed to oxygen, the decomposition temperature drops to 300°C so that temperatures well below the T_g of many polyimides, facilitate the foaming process. Although PMMA is more stable than both poly(propylene oxide) and PEO, it still provides a processing window of about 125°C for the foaming

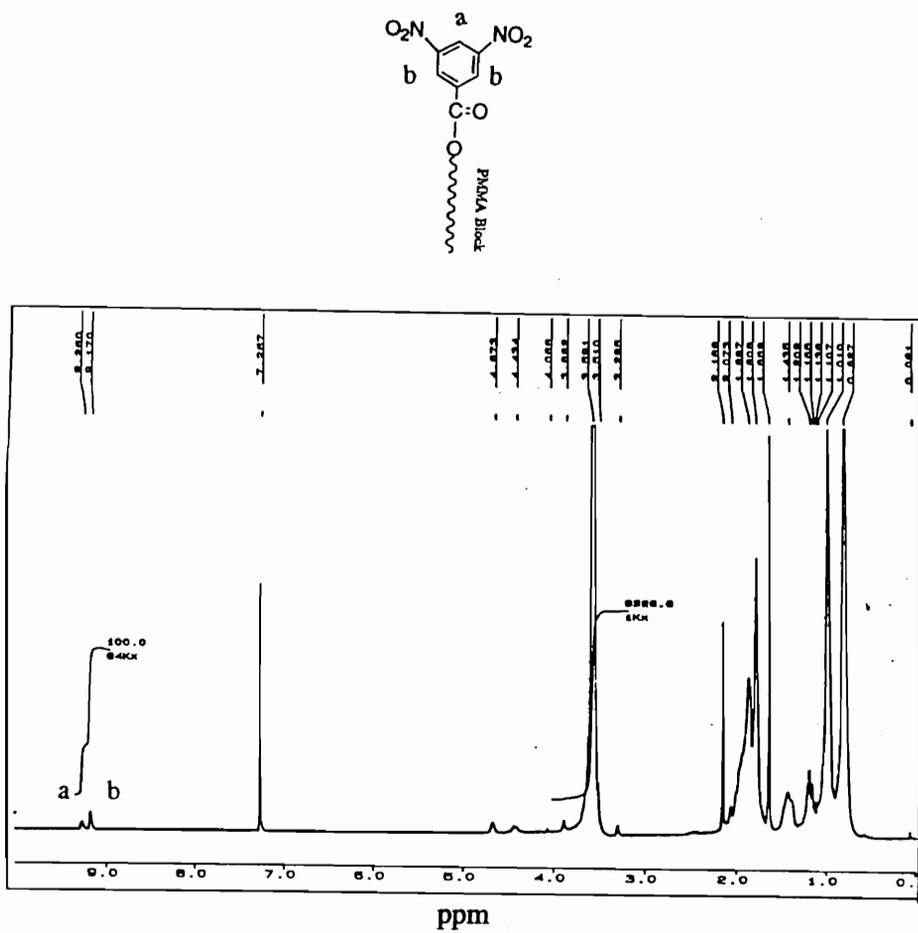


Figure 4.3.6.4 ¹H NMR Spectrum of Dinitro Benzoate Terminated PMMA

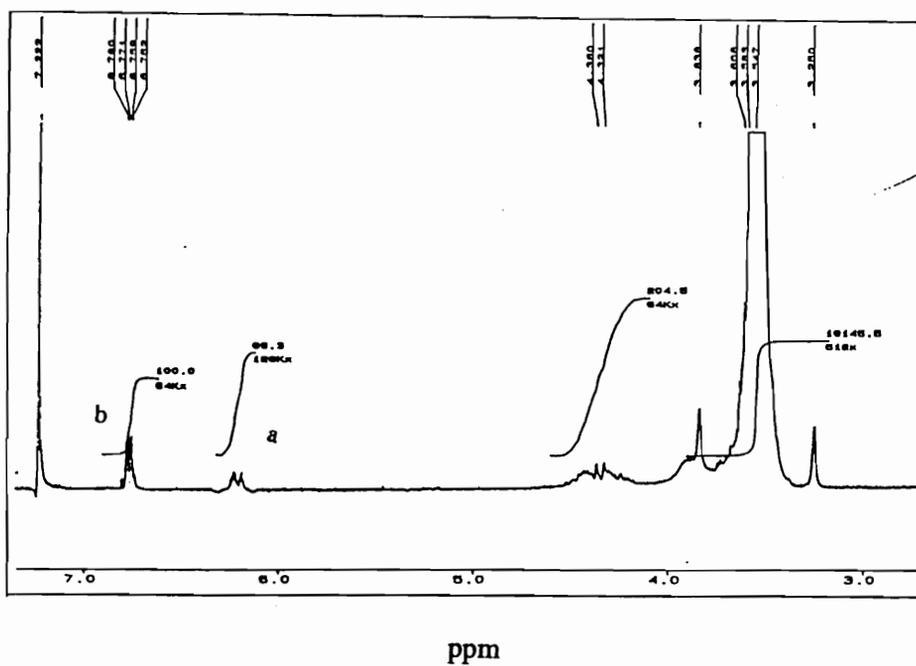
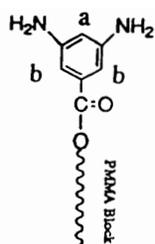


Figure 4.3.6.5 ^1H NMR Spectrum of Diamino Benzoate Terminated PMMA

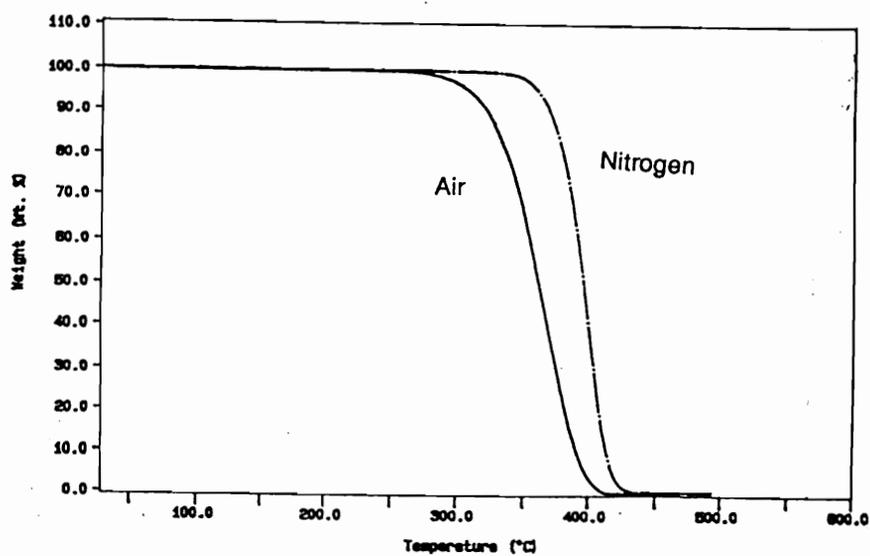
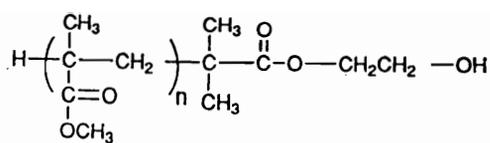


Figure 4.3.6.6 Dynamic TGA Spectrum of Hydroxy Terminated PMMA Oligomer
Synthesized via GTP in Both Air and Nitrogen

process and hence it was expected to produce stable polyimide foams upon thermal degradation of PMMA from the polyimide matrix.

In order to evaluate the feasibility of generating polyimide foam from the polyimide-PMMA copolymers, PMDA/3FDA polyimide-PMMA graft copolymers were synthesized. Diamine terminated PMMA of molecular weight 15,000 g/mole was used for the synthesis of the graft copolymers. The copolymer synthesis involved the addition of the solid PMDA to a solution of 3FDA and the diamine functionalized PMMA oligomer as described earlier. The reaction scheme for the synthesis of the copolymer is provided in Figure 4.3.6.7. The polymerization's were carried out in NMP at solid compositions of approximately 15 wt%, and were maintained at ambient temperature for 24 hours, yielding viscous solutions of the target poly(amic acid). Imidization of the poly(amic acid) solutions was accomplished by adding in excess acetic anhydride and pyridine in 6 - 8 hours at 80°C. The use of the diamine terminated PMMA oligomers afforded a graft copolymer, while the PMMA was grafted on the polyimide main chain. Polyimide-PMMA copolymer containing 25 wt.% of the PMMA labile block was prepared. Presence of any unreacted PMMA oligomers were completely removed by overnight stirring of the precipitated copolymer in hot THF. The composition of the PMMA in the copolymer was assessed by ¹H-NMR, through comparing aromatic protons of the polyimide to the aliphatic methyl protons of the PMMA methyl ester as shown in Figure 4.3.6.8, and by TGA, through measuring the weight retention after decomposition of the thermally labile block as shown in Figure 4.3.6.9. The composition of the PMMA incorporated into the copolymer was comparable to that initially charged as shown also in Table 4.3.6.2.

The processing window for film formation was established for 3FDA / PMDA / PMMA copolymer using ¹H NMR, TGA and dynamic mechanical measurements. In order to prepare polyimide films samples of PMDA / 3FDA / PMMA copolymers were dissolved in NMP and cast on to a glass plate. The glass plate was gradually heated at a rate of 5°C /

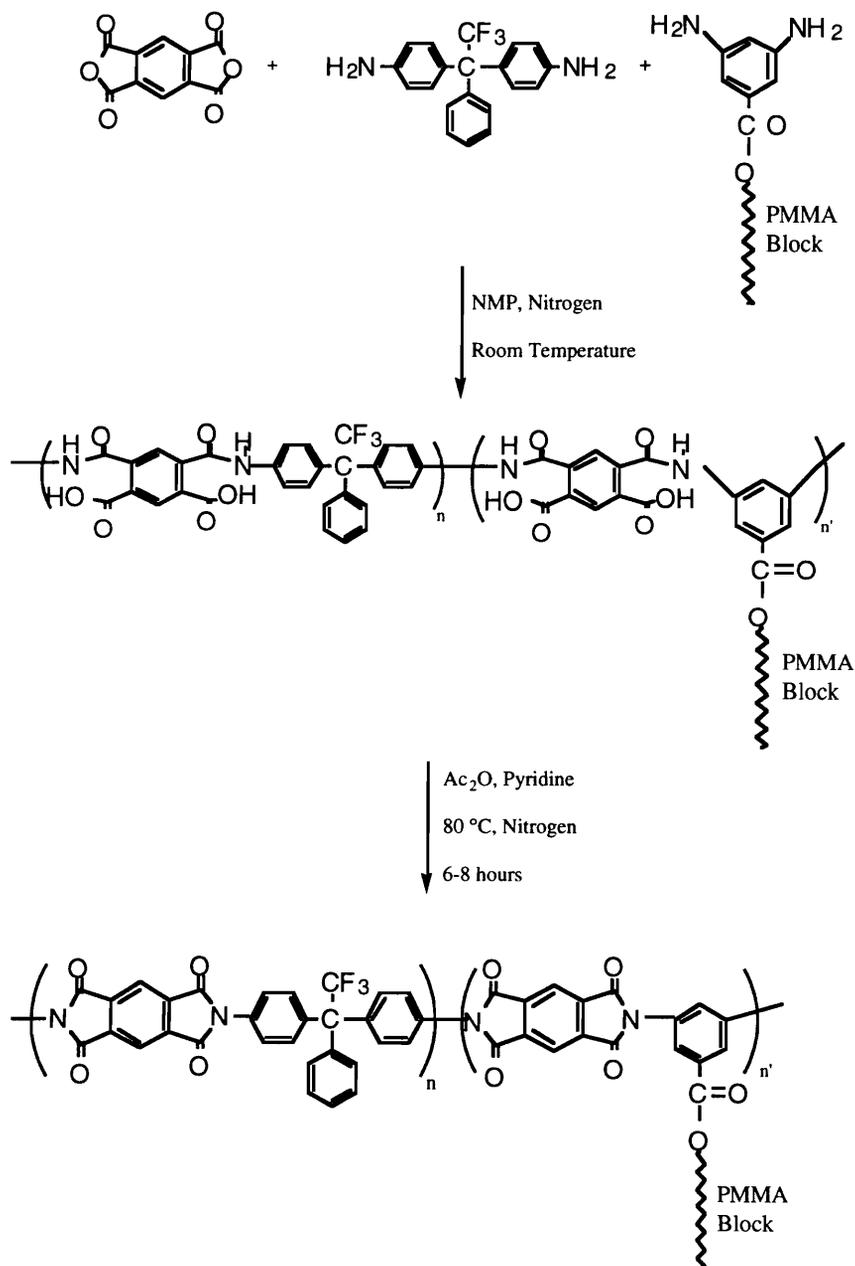


Figure 4.3.6.7 Synthesis of PMDA/3FDA Polyimide-PMMA Graft Copolymer

Table 4.3.6.2 Characteristics of PMDA/3FDA/Polyimide-Poly(methyl methacrylate)
Copolymer

Sample	Weight % of PMMA		
	Theoretical	From ¹ H NMR	From TGA
1	25	24.5	23.5

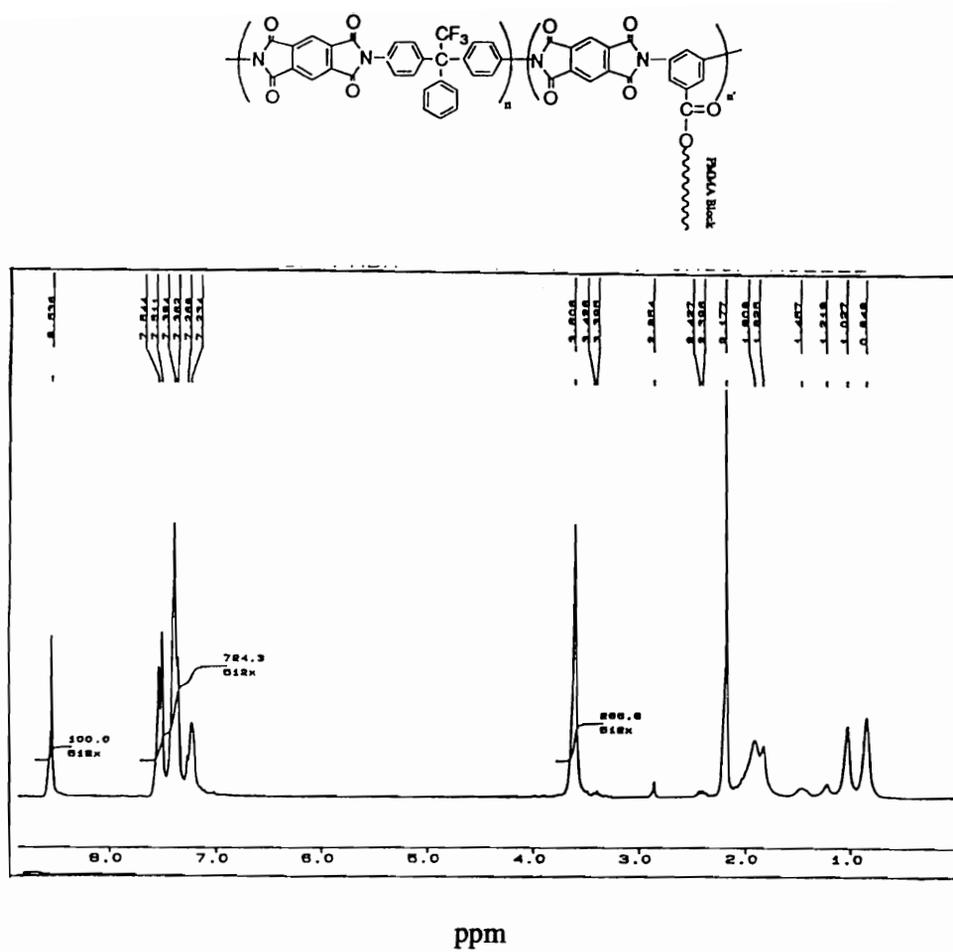


Figure 4.3.6.8 ¹H NMR Spectrum of PMDA/3FDA-PMMA Graft Copolymer

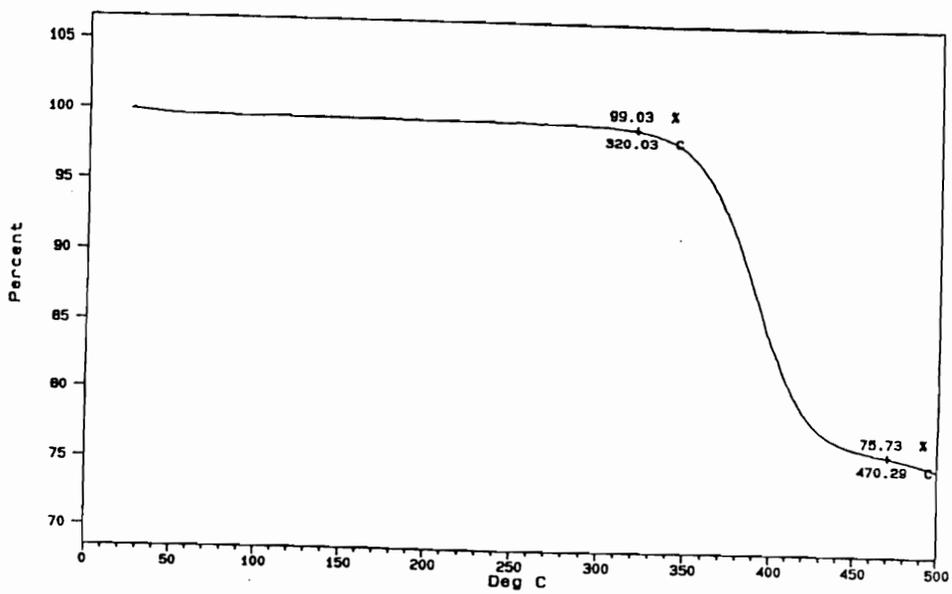
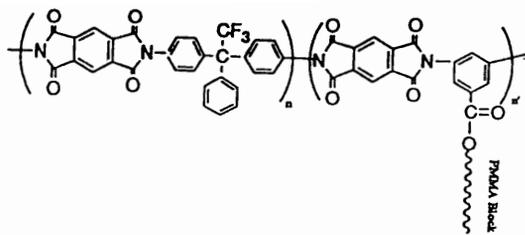


Figure 4.3.6.9 Dynamic TGA Thermogram of PMDA/3FDA-PMMA Graft Copolymer in air (heating rate 10°C/min)

process and hence it was expected to produce stable polyimide foams upon thermal degradation of PMMA from the polyimide matrix.

In order to evaluate the feasibility of generating polyimide foam from the polyimide-PMMA copolymers, PMDA/3FDA polyimide-PMMA graft copolymers were min to 300°C and held there for 1 hour under nitrogen atmosphere, which resulted in a clear polyimide-PMMA copolymer film. The ^1H NMR spectra of the samples cured at 300°C showed no detectable traces of the solvent (NMP). Moreover integration of the aromatic protons of the polyimide against the aliphaticmethyl protons of the PMMA methyl ester indicated no loss of the thermally labile PMMA under this condition. Thus it was clearly demonstrated that complete removal of the solvent NMP was achieved with minimal loss of PMMA.

The dynamic mechanical results for the imide-PMMA graft copolymers was performed on the copolymer films. Surprisingly, the copolymer exhibited only one transition, which could characterize a miscible system and not of a microphase separated system. The low temperature transition of the PMMA phase expected to occur near 110 to 115°C, was completely absent, and a higher temperature transition corresponding to that of the polyimide block which was expected to occur near 440°C was also absent. Instead, a single transition at 305°C was noted, which lies between the glass transition temperatures of the PMMA and polyimide homopolymers. This result is provided in Figure 4.3.6.10. This transition at 305°C might be due to, a) degradation of the PMMA labile block and the resulting by-products plasticizing the polyimide matrix and suppressing the glass transition temperature of the polyimide phase, or b) the complete miscibility between the polyimide phase and the PMMA phase. The absence of the lower transition of the PMMA phase and the presence of a single transition suggests miscibility between the two systems, which requires further investigation into this system.

It is well known that casting solvents play an important role in obtaining phase separated morphology . In an attempt to obtain phase separated morphology in the case of

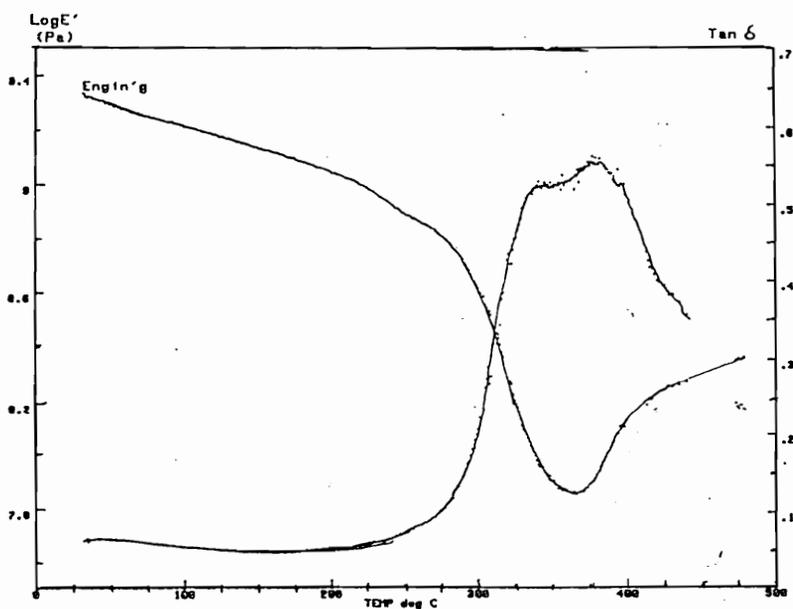
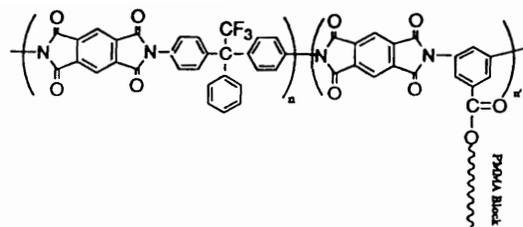


Figure 4.3.6.10 Dynamic Mechanical Spectrum of PMDA/3FDA-PMMA Graft Copolymer
Cast from NMP

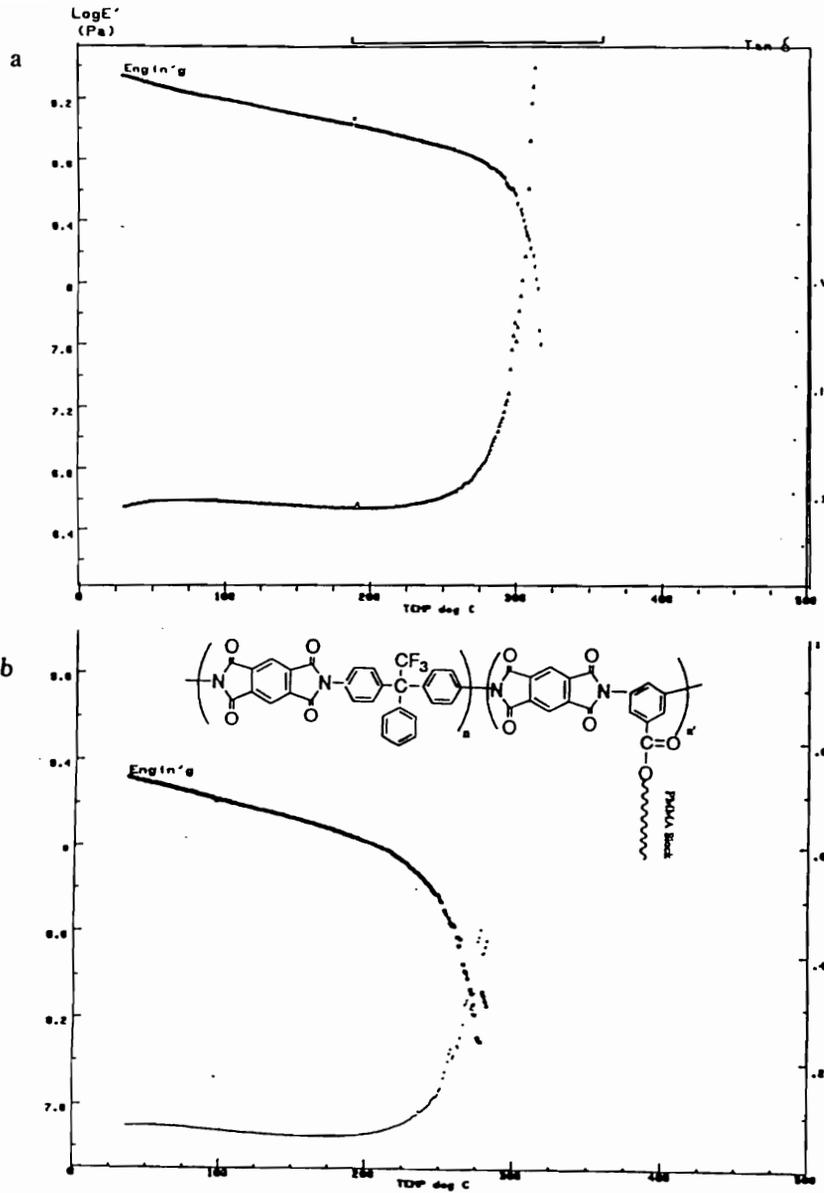


Figure 4.3.6.11 Dynamic Mechanical Spectrum of PMDA/3FDA-PMMA Graft Copolymer
Cast from a) DMAc and b) DMPU

PMDA/3FDA polyimide-PMMA graft copolymers, films were cast from two different solvents (apart from NMP). A PMMA-polyimide copolymer was dissolved in DMAc and N,N'-dimethylpropyleneurea (DMPU), cast on to a glass plate, and heated at a rate of 5°C / min to 300°C and held there for 1 hour under nitrogen atmosphere. Films from both solvents resulted in a clear polyimide-PMMA copolymer film. Dynamic mechanical analysis was performed on these films and, once again, the copolymer exhibited only one $\tan \delta$ peak in both cases. The low temperature transition of the PMMA phase, expected to occur near 110 to 115°C, was once again absent. The transition was observed at around 315°C when DMAc was used, and at approximately 295°C when DMPU was used as the solvent. However, in both cases, the $\tan \delta$ peak was observed to occur between the glass transition temperatures of the PMMA and polyimide homopolymers as in the case of the films prepared from NMP. These results further indicate that the PMMA-polyimide is forming a miscible system irrespective of the solvent used to cast the copolymer film. Figure 4.3.6.11 shows the dynamic mechanical analysis results of the copolymer cast from both DMAc and DMPU are provided in Table 4.3.6.3.

Thus, when varying the casting solvents failed to produce phase separated films, other options such as mixing in higher molecular weight PMMA homopolymer with the graft copolymer, was investigated. It was believed that by mixing in the higher molecular weight PMMA with the copolymer, PMMA-PMMA interaction could be promoted, and this should facilitate the phase separation of the PMMA block of the copolymer. To test this hypothesis, PMDA/3FDA polyimide-PMMA graft copolymer was dissolved in NMP, to this 43000 g/mole PMMA homopolymer was added (into NMP) such that the ratio of the PMMA homopolymer to the PMMA present in the copolymer was 0.1. After complete dissolution of the homopolymer and copolymer, films were cast on to a glass plate and heated up to 300°C, in nitrogen atmosphere. The films were once again observed to be yellow and transparent. Dynamic mechanical analysis of the film once again indicated a

Table 4.3.6.3 Characteristics of PMDA/3FDA Polyimide-PMMA Films Cast from Different Solvents

Casting Solvents	Physical Appearance of Films	T _g obtained from DMTA (°C)
NMP	Yellow & Transparent	305
DMAc	Yellow & Transparent	315
DMPU	Yellow & Transparent	295

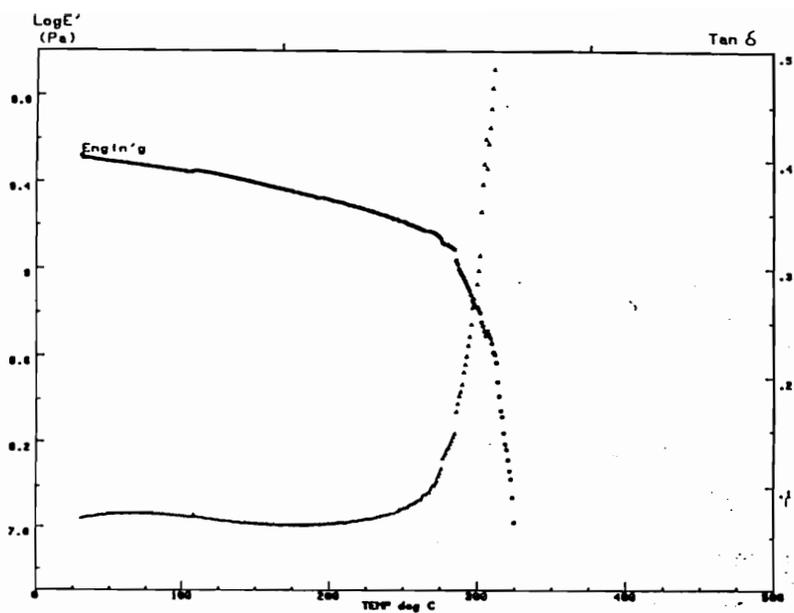


Figure 4.3.6.12 Dynamic Mechanical Spectrum of PMDA/3FDA-PMMA Graft Copolymer/ PMMA Homopolymer Blend Cast From NMP

single $\tan \delta$ peak around 300°C, indicating no phase separation. It should be noted that increasing the ratio of the PMMA homopolymer to the PMMA in the copolymer to 0.5, while simultaneously increasing in the molecular weight of the PMMA homopolymer to 93,000 g/mole, failed to produce phase separated films. Once again, DMTA analysis of the film indicated only one T_g and the transition was observed to further decrease in temperature to about 240°C. These results are provided in Figure 4.3.6.12.

In order to prove that the PMDA/3FDA polyimide was truly miscible with poly (methyl methacrylate) oligomers, the two homopolymers were physical blended. This blend of the polyimide-PMMA homopolymers, (PMMA molecular weight 15,000 g/mole) was performed by dissolving the two homopolymers (polyimide / PMMA : 75 / 25 wt.% ratio) in NMP and casting the homogeneous solution on a glass plate. Films of the homopolymer blends were prepared by heating the solution to 300°C and holding it there for 1 hour under nitrogen atmosphere. Yellow transparent films were obtained. Dynamic mechanical analysis of the film indicated one transition as expected at around 300°C, which was very close to the transition observed for the graft copolymer. Dynamic mechanical spectrum of the physical blend is provided in Figure 4.3.6.13.

Realizing that the PMDA/3FDA polyimide forms miscible blend with 15,000 g/mole PMMA oligomer, the effect of molecular weight of PMMA and composition of the blend on glass transition temperature were investigated. In order to study the effect of composition on the glass transition temperature of the blend, physical blends of PMDA/3FDA homopolyimide and 8000 g/mole GTP polymerized PMMA were dissolved in NMP in 75 / 25, 65 / 35 and 50 / 50 weight percents respectively. The samples were cast on a glass plate and heated under nitrogen to 300°C and held there for 1 hour. The films were peeled from the glass plate for thermogravimetric analysis dynamic mechanical analysis. All the films were observed to be yellow and transparent. TGA experiment was

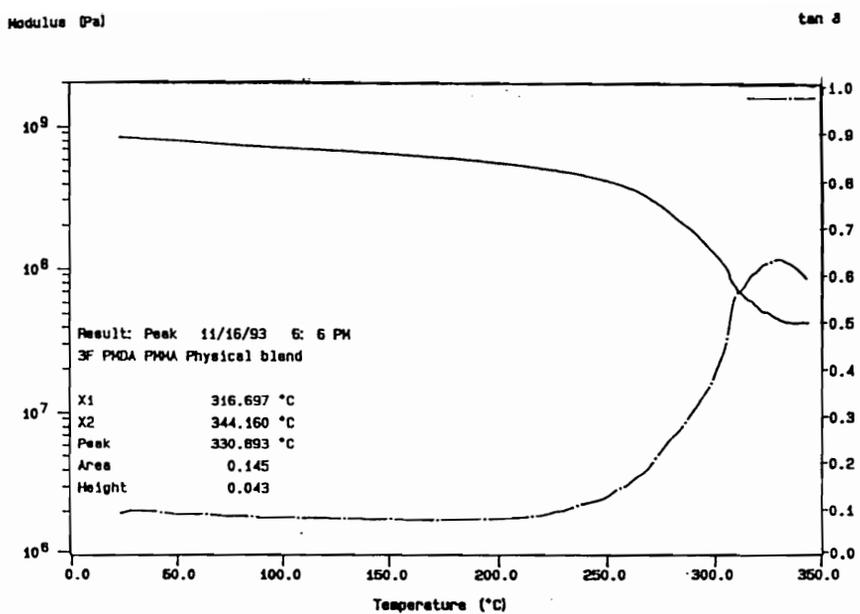


Figure 4.3.6.13 Dynamic Mechanical Spectrum of PMDA/3FDA-PMMA Physical Blend

Cast from NMP

performed on the films to conform the weight percent of the PMMA in the blend prepared. Close agreement was observed between the target weight percent and that observed from TGA experiment as can be observed in Table 4.3.6.4. DMA measurements in air at 1Hz indicated only one tan δ peak as expected, and this peak was observed to go down in temperature from 330 to 215°C, and on increasing the amount of PMMA in the polyimide matrix from 25 wt.% to 50 wt.%. The change in T_g was observed to follow closely with the Flory-Fox equation of²¹⁰

$$1/T_g = \{w_1/T_{g1}\} + \{w_2/T_{g2}\}$$

where T_g corresponds to the glass transition temperature of the physical blend; w₁ and w₂ are the weight fractions of the polyimide and the PMMA homopolymers in the blend; while the T_{g1} and T_{g2} are their corresponding T_g's in kelvin. The dynamic mechanical spectrum of the effect of composition on glass transition temperature is provided in Figure 4.3.6.14. These results are also tabulated in Table 4.3.6.4.

In order to study the effect of PMMA molecular weight on the glass transition temperature of the physical blends, the composition of the polyimide-PMMA was fixed to 50:50 wt.% and the molecular weight of PMMA varied from 8000 g/mole to 15,000 g/mole to 40,000 g/mole. Films of the respective physical blends were prepared as described previously by dissolving the individual samples in NMP and casting the homogeneous solution on to a glass plate. The plate was heated to 300°C and held there for 1 hour under nitrogen atmosphere. DMTA performed on all three films again exhibited only one transition, which occurred in all cases at around 215°C. Thus changing the molecular weight of PMMA had no effect on the glass transition of the blend. But interestingly PMMA was observed to be miscible up to 40,000 g/mole in molecular weight with the PMDA/3FDA polyimide. The dynamic mechanical spectrum showing the effect of varying the PMMA molecular weight on the glass transition temperature of the polyimide-PMMA physical blend is provided in Figure 4.3.6.15. It should be noted that the tan δ peak was

Table 4.3.6.4 Effect of PMDA/3FDA Polyimide-PMMA Composition on the Glass Transition Temperature of Physical Blend

Sample		Mol. Wt. of PMMA	Wt. % of PMMA by TGA	Physical appearance of Film	T _g by DMA (°C)	Cal. T _g by Flory-Fox Eq.
Wt. % of Polyimide	Wt. % of PMMA					
100	0	-	-	Yellow	450°C	-
0	100	8000	-	white powder	108	-
75	25	8000	26	Yellow / Transparent	330	317
65	35	8000	34.5	''	309	277
50	50	8000	50	''	215	226

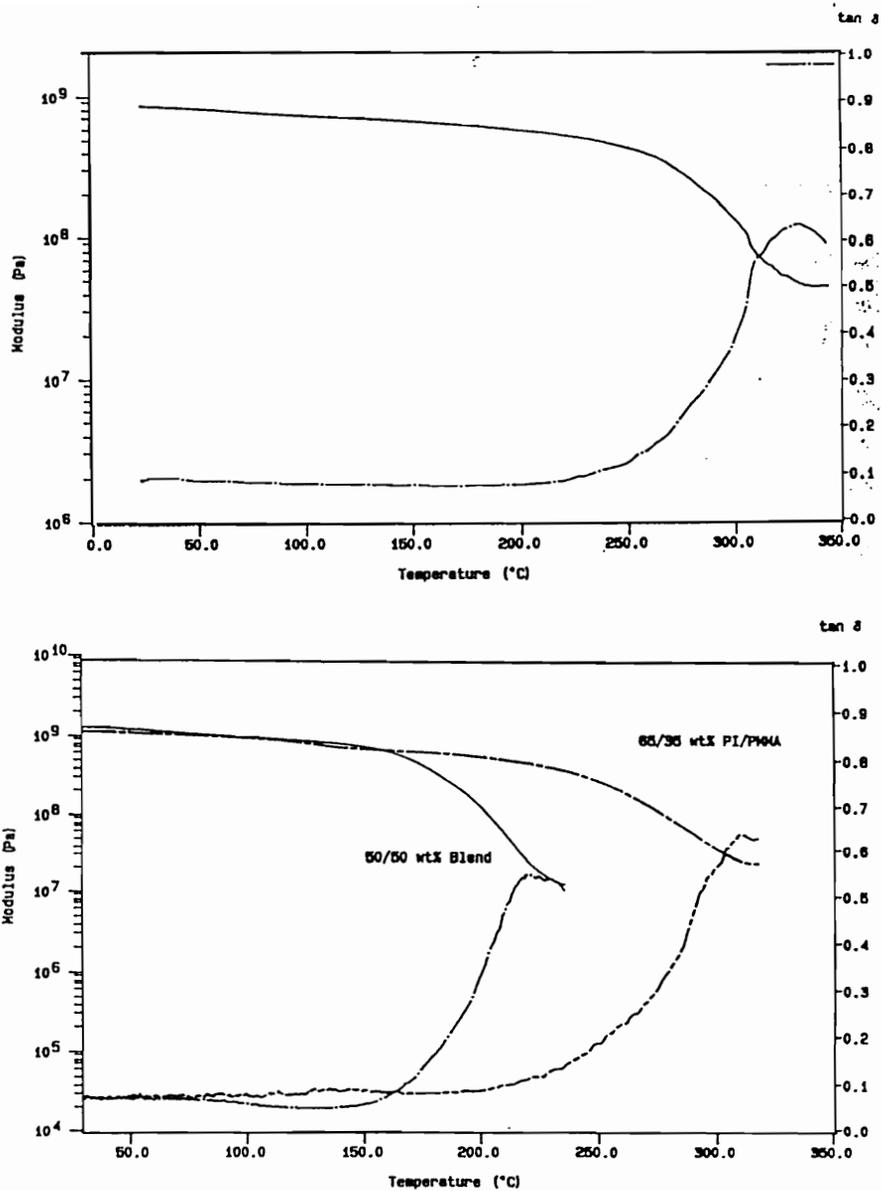


Figure 4.3.6.14 Dynamic Mechanical Spectrum of PMDA/3FDA-PMMA Physical Blend:
Effect of Varying PMMA Composition on T_g of the Blend

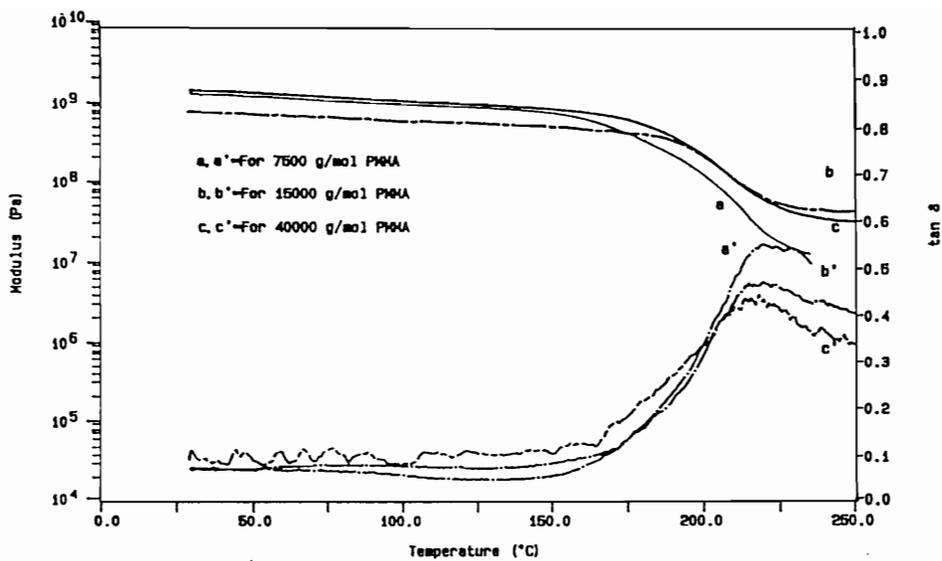


Figure 4.3.6.15 Dynamic Mechanical Spectrum of PMDA/3FDA-PMMA Physical Blend:
Effect of Varying PMMA Molecular Weight on T_g of the Blend

Table 4.3.6.5 Effect of PMMA Molecular Weight on the Characteristics of Polyimide-
PMMA Physical Blend

Sample		Mol. Wt. of PMMA	Wt. % of PMMA by TGA	Physical appearance of Film	T _g by DMA (°C)	Cal. T _g by Flory-Fox Eq.
Wt. % of Polyimide	Wt. % of PMMA					
100	0	-	-	Yellow	450°C	-
0	100	8000	-	white powder	108	-
50	50	8000	51	Yellow / Transparent	215	226
50	50	15000	51	''	213	226
50	50	40000	50	''	213	226

observed to become increasingly broader, when the molecular weight was increased . These results are also provided in Table 4.3.6.5

In order to determine whether PMMA generally forms miscible blend with all polyimides, in general the structure of the polyimide was varied systematically by synthesizing them with different dianhydride units but the same diamine unit (i. e. 3FDA). The homopolyimides (apart from the PMDA/3FDA system), synthesized were BPDA/3FDA polyimide, BTDA/3FDA polyimide, 6FDA/3FDA polyimide, and ODPA/3FDA polyimide. These were all synthesized using the standard two-step polyimide synthesis which involves the formation of poly(amic acid), followed by cyclization to polyimides using chemical imidization techniques. The intrinsic viscosity of all the polyimide was observed to be around 0.3 dl/g at 25°C in NMP. In order to prepare a physical blend with PMMA, the 40,000 g/mole PMMA polymer was dissolved with the respective homopolyimide in NMP. The films were then cast on to a glass plate and heating up to 300°C under nitrogen atmosphere. Homopolyimide samples containing two different wt.% of PMMA, 25 and 50%, were prepared. Poor opaque films were obtained from BPDA/3FDA polyimide-PMMA physical blends containing both 25 and 50 wt.% of PMMA and also in the case of the ODPA/3FDA polyimide-PMMA blend having higher wt.% of PMMA. The poor quality of the films prevented us from performing dynamic mechanical analysis on the films. However, the films opaqueness indicated possible gross phase separation. In the case of the 6FDA/3FDA polyimide - PMMA blend, samples were observed to be transparent in nature. The dynamic analysis of the films containing 25 and 50 wt.% of PMMA exhibited two peaks indicative of phase separated morphology. A low temperature transition of the PMMA phase was observed at 135°C, irrespective of the wt.% of PMMA, while the high temperature transition corresponding to the polyimide phase, was observed to decrease from 305 to 265°C on increasing the PMMA composition from 25 to 50 wt.%. The T_g of the 6FDA/3FDA homopolyimide has been reported to be around

314°C by DSC. Similarly, BTDA/3FDA polyimide-PMMA blend containing 50 wt.% of PMMA, and ODPA/3FDA polyimide-PMMA blend containing 25 wt.% of PMMA exhibited two transitions, also indicating of phase separated morphology. In the case of the BTDA/3FDA polyimide-PMMA blend, a low transition temperature for the PMMA phase was observed at 126°C, while a high transition temperature corresponding to the polyimide phase was observed at around 255°C. For ODPA/3FDA polyimide-PMMA blend, the low transition temperature was observed to approximately 130°C while the higher transition temperature for the polyimide phase was observed at around 290°C. These results are provided in Table 4.3.6.6 and in Figures 4.3.6.16 to 4.3.6.18.

Based on earlier result with respect to the PMDA/3FDA-PEO graft copolymers, in which partial miscibility prevented the foam generation on degradation of the PEO phase, foam formation was not anticipated from the PMDA/3FDA-PMMA materials due to miscible nature of this system. Hence, no attempt was made to generate foam from this copolymer.

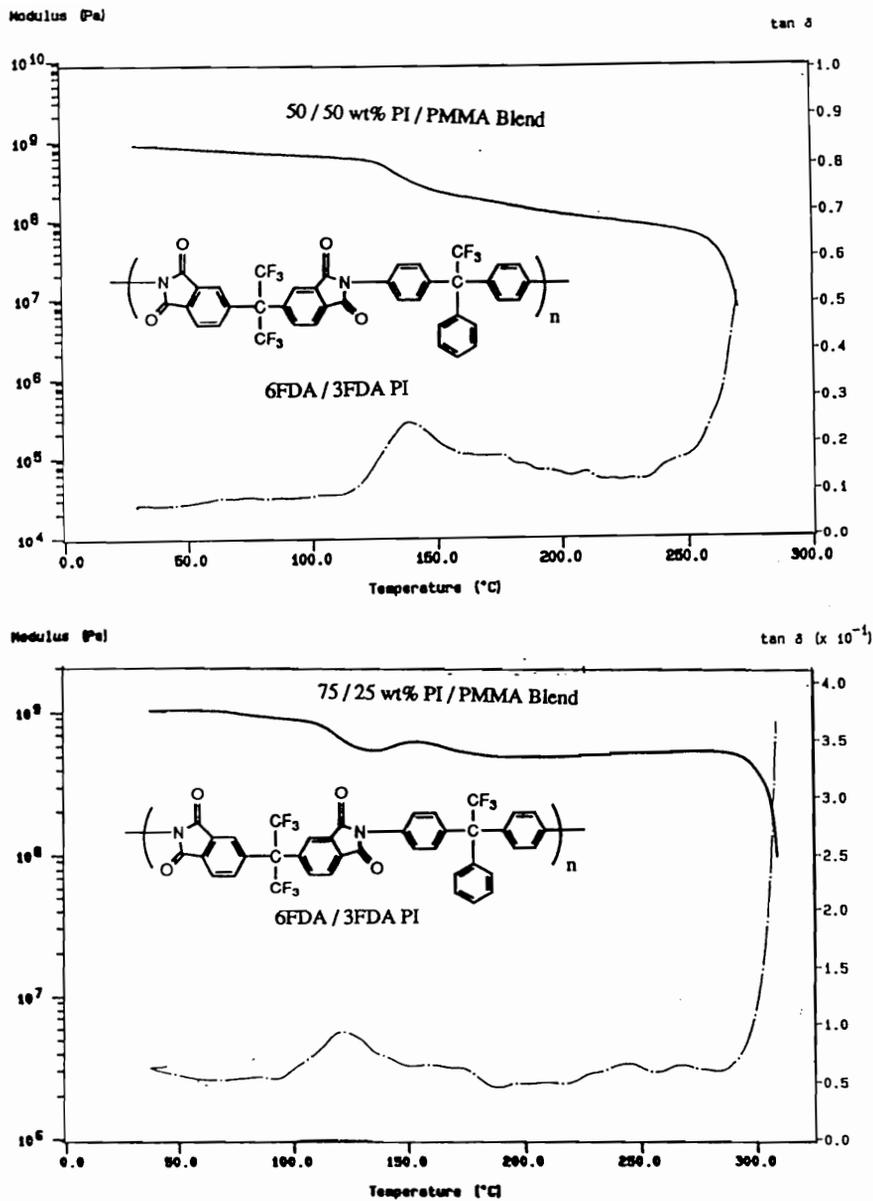


Figure 4.3.6.16 Dynamic Mechanical Spectrum of 6FDA/3FDA-PMMA Physical Blend

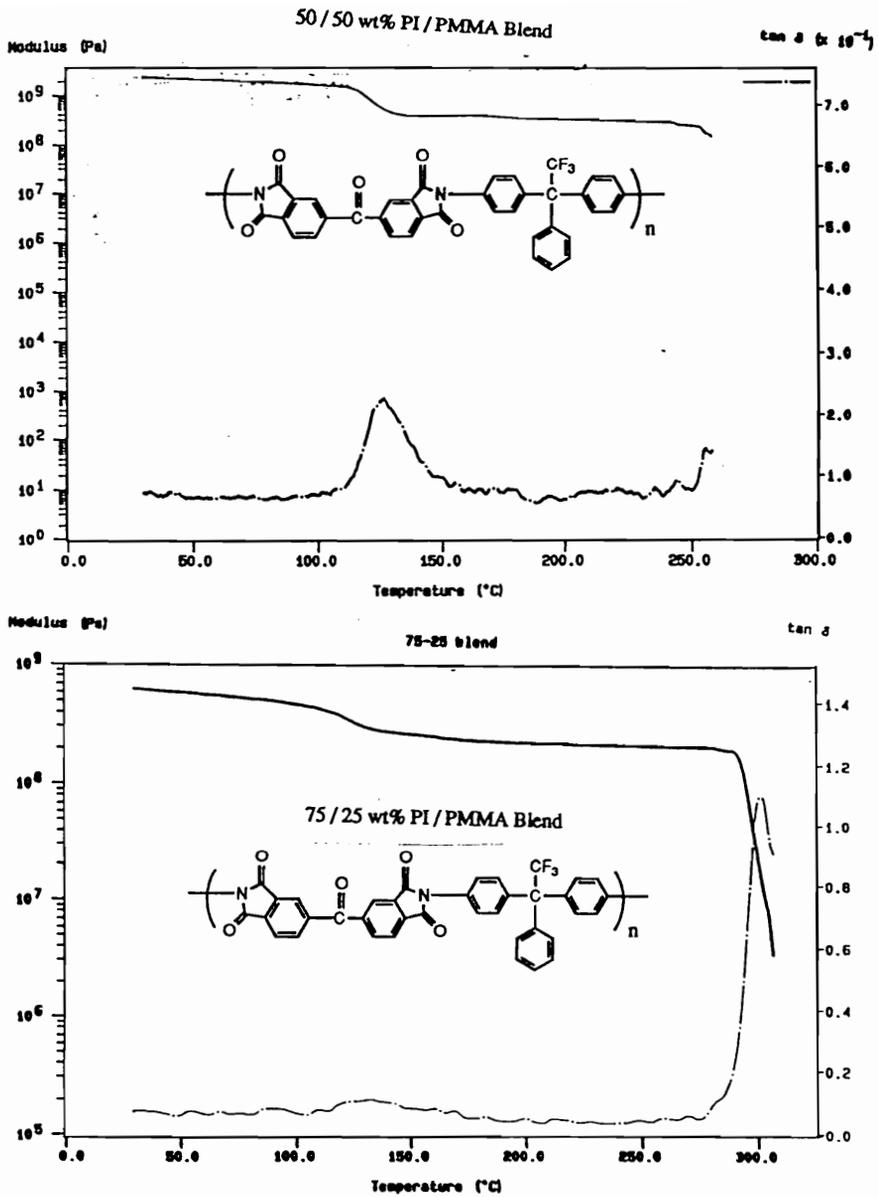


Figure 4.3.6.17 Dynamic Mechanical Spectrum of BTDA/3FDA-PMMA Physical Blend

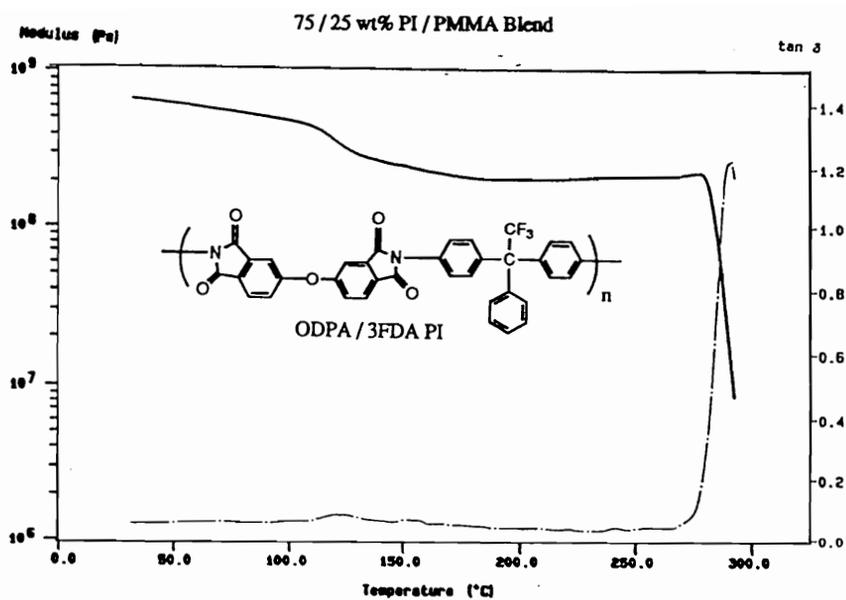


Figure 4.3.6.18 Dynamic Mechanical Spectrum of ODPA/3FDA-PMMA Physical Blend

Table 4.3.6.6 Effect of Polyimide Structure on the Characteristics of Polyimide-PMMA
Physical Blend

Sample	[h] of homopolyimide at 25°C in NMP (dl/g)	Mol.Wt. of PMMA (g/mole)	Wt. % of PMMA	T _g of the blend by DMA (°C)		Physical appearance of film
PMDA/3FDA	0.663	40,000	50	-	213	yellow / transparent
6FDA/3FDA	0.293	40,000	50	137	265	clear / transparent
		40,000	25	135	305	' '
BTDA/3FDA	0.295	40,000	50	126	255	opaque
ODPA/3FDA	0.277	40,000	50	-	-	poor film
		40,000	25	130	290	opaque
BPDA/3FDA	0.294	40,000	25	-	-	poor film

5.0 — CONCLUSIONS

A new method of preparing polyimide foams with pore sizes in the nanometer range has been demonstrated. Microphase separated block and graft copolymers, comprised of a thermally stable polyimide as the continuous matrix phase and a thermally labile material, were prepared. The copolymers were designed to allow conventional electronic packaging solvent processing (spin coating, doctor blading, etc.) and when thermally treated, the labile phase experienced thermolysis, resulting in pores whose size and shape were dictated by the initial multiphase block copolymer morphology. Triblock copolymers comprised of 3FDA/PMDA polyimides and poly(propylene oxide) as the thermally decomposable end blocks were studied. Fully cyclized soluble 3FDA/PMDA imide-propylene oxide multiphase copolymers were prepared via the poly(amic acid) precursor route, followed by imidization. The propylene oxide composition was controlled to ≤ 20 volume % discrete domains of the thermally labile component in the polyimide matrix. Microphase separated morphologies were observed by dynamic mechanical analysis for all the copolymers. Films were solvent cast from NMP, cured and the processing window for film and foam formation was determined by $^1\text{H-NMR}$, TGA and dynamic mechanical analysis methodologies. The generation of nanofoams was accomplished by subjecting the copolymer films to thermal treatment in air (240°C or 270°C for 10 hours), followed by 300°C for 2 hours, which quantitatively degraded the labile propylene oxide block. Microscopy (TEM), scattering (SAXS), and density measurements were used to characterize the foam formation. The density values ranged from 9 to 18% less than the polyimide homopolymers, which was consistent with foam generation. These results indicate that successful foam generation is influenced by the plasticization of the polyimide matrix by the volatile degradation by-products of the labile propylene oxide component. Observed differences in density values relative to starting compositions were attributed to

possible plasticization of the polyimide matrix by acetone and acetaldehyde degradation products of the propylene oxide block.

Processing of thin films from completely cyclized 3FDA/PMDA copolymers by conventional spin coating techniques was difficult and better results were achieved via a poly(amic alkyl ester) method. The higher solubility of the poly(amic alkyl ester) copolymers (especially the meta isomer) in polar aprotic solvents, compared to the corresponding fully cyclized polyimides permitted high solids content formulations to be prepared in a DMF/2-ethoxyethyl acetate solvent mixture. Spin casting on a silicon substrate and thermal treatment for 1 hour at 300°C under inert atmosphere produced good films. Thus, both imidization of the poly(amic alkyl ester) and subsequent solvent removal was accomplished at temperatures below the decomposition temperatures of the labile block in nitrogen. This procedure afforded the microphase separated copolymer thin films. The synthesis and characterization of the nanofoams was achieved in the same manner as for the procedure where the polyimides were obtained from the fully cyclized 3FDA/PMDA copolymers. Density values were observed to be 13-16% less than those of the polyimide homopolymer, which is again consistent with foam generation. The ability to generate thin films via the poly(amic alkyl ester) route provided further opportunities to define the properties of the foamed materials, such as thin film stress and refractive index. Refractive index values were 0.08 to 0.18 less than those of the polyimide homopolymer, which would be expected from the foams. Thin film stress was desirably also observed to be 40-50% less than for the polyimide homopolymer.

Thermosetting polyimide nanofoams were generated in an attempt to decrease the interaction between the degradative by-products and the polyimide matrix, and also to possibly increase the volume fraction of pores obtainable. Applying this strategy required careful balancing of the crosslinking process with simultaneous solvent removal, so that minimal degradation of the labile component occurred prior to the foaming step. Poly(amic

alkyl ester) copolymers with both terminal and pendent ethynyl groups were synthesized. Crosslinking, imidization of the poly(amic alkyl ester), and solvent removal were all accomplished in a single step, by casting from NMP, heating to 300°C in an inert atmosphere, and post-curing for 3 hours at 300°C. The processing window for film and foam formation was identified by TGA and dynamic mechanical analysis. Foams were generated by subjecting the crosslinked copolymers to thermal treatment in air at 270°C for 10 hours. The formation of pores was verified by TEM, SAXS and density measurements. Density values were observed to be 11-25% less than the homopolyimides in the case of the crosslinked materials obtained from terminal ethynyl groups, and 23-60% less than those for the ethynyl based pendant crosslinked materials. TEM measurements indicated that the structure of the resulting nanofoams was larger than those obtained from the uncrosslinked, completely cyclized polyimide copolymers. Unfortunately, these materials were brittle and difficult to process as thin films using standard spin coating techniques.

Poly(ethylene oxide) and poly(methyl methacrylate) mono functional oligomers prepared via anionic and group transfer polymerization (GTP), respectively, were also used as labile blocks for polyimide nanofoams. Graft copolymers of poly(ethylene oxide)/3FDA-PMDA polyimide and poly(methyl methacrylate)/3FDA-PMDA polyimides were prepared via the poly(amic acid) precursor route, followed by imidization. Once again, the composition of the labile component was deliberately maintained at low levels in order to produce discrete domains of the labile component in the high temperature polymer matrix. Microphase separated morphology was observed by dynamic mechanical analysis for copolymers containing PEO as the labile component, while, surprisingly, no such phase separated morphology was observed for copolymers containing PMMA as the labile component. The T_g of the PEO phase was observed to be around -8°C, as compared to -50°C reported in the literature, while the T_g of the polyimide phase decreased to 377°C

from 420°C for the homopolyimide, indicating substantial phase mixing. Efforts to generate foams from the polyimide/PEO copolymers were unsuccessful, as indicated by density and TEM measurements. Copolymers containing PMMA as the labile component demonstrated a compositionally dependent single glass transition temperature, thus indicating a miscible system. Similar results were also noted for the 50:50 PMMA/3FDA-PMDA homopolymer blends. Thus, no attempt was made to generate foams from the systems containing PMMA as the labile block, but additional fundamental research on this apparently novel physical blend should be considered.

6.0 - SUGGESTED FUTURE STUDIES

Many future directions exist for the various aspects of this research involving the development of nanofoams using the block and graft copolymer approach. Some of these areas which deserve attention will be highlighted below.

- 1) Studies directed towards identifying 3FDA/PMDA based lower dielectric polyimide matrix to reduce the dielectric constant and water absorption of the base polyimide. This can be effectively accomplished without the loss of the solubility or the high T_g of the base material by incorporating fluorine groups on the backbone of the polyimide. Thus foaming this highly fluorinated base polyimide further reduction in dielectric constant can be expected i.e. towards the ultimate goal of a dielectric constant of 2.
- 2) Development of better labile block is very much necessary. Labile blocks that would allow the processing of the polyimide, but that would degrade more efficiently and cleanly with less interaction with the polyimide matrix in an inert atmosphere has to be developed for this concept to used in an actual chip manufacture. Labile blocks such as poly(ethylene carbonates), poly(butylene-sulfur dioxide) copolymers can be tried.
- 3) Interestingly it was observed that PMMA forms a miscible blend with the 3FDA/PMDA polyimide matrix. Studies on this material should be pursued further to obtain phase diagrams of this miscible system. Also attempts can be made to use poly(*n*-butyl methacrylate) a more hydrophobic polymer, as a labile block. Copolymers of this material with small amounts of chloro ethacrylate or cyano ethacrylate should provide us with labile blocks that could degrade at lower temperatures even in an inert atmosphere.

7.0 - REFERENCES

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VITA

Saikumar Jayaraman, son of Kamakshi and Jayaraman, was born October 14, 1965 in Madras, India. He graduated from Santhome Hr. Sec. School in June of 1983, and began his undergraduate studies at P.S.G. College of Technology as a Applied Science major and received his B. Sc. degree in June of 1986. Though initially his interests was directed towards medicinal field, exposure to an elective class in the field of polymer science during the final year of undergraduate studies opened a new avenue of pursuit. In August of 1986, he entered the graduate program in polymers at the Madras Universities Department of Polymer Science, and receive his M.Sc. in Polymer Science in June of 1988. After a short period in industry, he continued his studies by joining graduate program at the chemistry department of Wright State University in June of 1989, where he worked on synthesizing and characterizing Bismaleimide resins under the guidance of Dr. Ivan J. Goldfarb. After receiving his Master of Science degree in August of 1991, he entered the graduate program at Virginia Polytechnic Institute to work towards his goal of obtaining a Doctorate degree. In the summer of 1992, he worked at IBM, Almaden Research Center, San Jose, Ca. His graduate research efforts at VPI under the guidance of James E. McGrath focused on developing phenyl ethynyl based matrix resins and on polyimide foams.

Saikumar Jayaraman has accepted a post-doctoral position in the Corporate Research and Development Center at B. F. Goodrich in Brecksville, Ohio.